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ISOTOPE EFFECTS IN THE COMBUSTION OF CARBON MONOXIDE[1]

BY R. W. ATTREE, F. BROWN, G. E. DUNN,[2] AND M. LOUNSBURY

ABSTRACT

The relative rates of reaction of $C^{12}O$, $C^{13}O$, and $C^{14}O$ with oxygen have been measured. When the oxidation proceeds mainly on the walls of the containing vessel the relative rates for $C^{13}O$ and for $C^{14}O$ compared to $C^{12}O$ are respectively 0.985 and 0.959. When reaction proceeds mainly in the gas phase there is no isotope effect within experimental error.

INTRODUCTION

In this investigation the relative rates of combustion of $C^{12}O$, $C^{13}O$, and $C^{14}O$ in oxygen have been studied. The object was to see whether a study of isotope effects could contribute to the understanding of the mechanism of the reaction and more generally to explore the possibility of using isotope effects to investigate gas phase reactions.

The reaction between carbon monoxide and oxygen has been thoroughly investigated (e.g. (6) and references to be found in (6)) and its main features are well known. It is a chain reaction which shows upper and lower pressure limits of explosion and is generally believed to proceed either on the wall of the containing vessel ('slow' reaction) or homogeneously (fast or explosive reaction) according to conditions.

The initiation of explosion by heating the mixed gases in a vessel requires a fairly high temperature, between 500 and 700° C., while the 'slow' reaction taking place on the walls proceeds quite rapidly at temperatures just below the explosion temperature. Mixtures of suitable proportion can be readily exploded by an electric spark. Many other variations in conditions are possible; e.g. admitting a cold mixture to a hot vessel; or mixing the two preheated gases. In general, the chief effect of varying the conditions is to change the relative importance of the heterogeneous and homogeneous reactions.

As an initial step in this investigation the principal features of previous work were repeated in order to test the apparatus and to establish the conditions for thermally induced explosion, slow reaction, spark induced explosion, etc.

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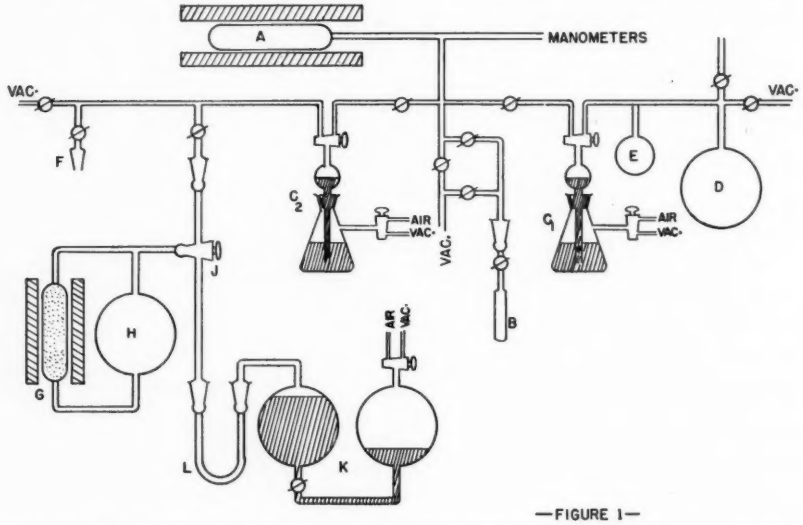
Good agreement was found on points where direct comparison was possible and it is not proposed to describe this part of the work in detail.

The method employed for measuring the isotope effects can be summarized as follows. A supply of carbon monoxide was prepared by complete reduction of carbon dioxide with hot zinc (1). Various types of combustions were carried out using a deficiency of oxygen so that the monoxide was only partially oxidized (usually about 30%). The carbon isotopic compositions of the dioxide samples so produced were then compared mass spectrometrically with that of the initial dioxide from which the monoxide was prepared. Thus the isotopic composition of the monoxide at the start of each reaction and the isotopic composition of the dioxide produced by its partial oxidation were known. By simple pressure measurements the amount of monoxide which had reacted was determined. The relative rates of combustion of $C^{12}O$, $C^{13}O$ (and $C^{14}O$ if present) can be obtained from these data. In the first experiments natural carbon dioxide was the starting material so that only the isotope effect for C^{13} compared with C^{12} was studied. Later the experiments were repeated starting with dioxide containing about one per cent C^{14} so that the effects for both C^{13} and C^{14} could be studied. Details of the experimental methods are given below.

EXPERIMENTAL

The main features of the apparatus are shown in Fig. 1. The silica reaction vessel *A* with volume about 100 ml. was heated by an electric furnace. Its temperature was measured by a thermocouple placed inside the furnace tube



—FIGURE 1—

against the outer wall of the reaction vessel. Samples of gas from the reaction vessel could be collected in a sampling tube *B*. The pressure in the furnace was measured by two manometers, the first being a simple mercury barometer type and the other a U-tube filled with Kel-F polymer grade 10. In the latter

case both arms of the U-tube could be opened to the system and then with one arm closed the manometer would indicate any pressure changes which occurred subsequently. The fluorocarbon polymer Kel-F has the advantages of high density and low vapor pressure but its high viscosity means that readings take rather a long time. The manometer, connections, stopcocks, etc. associated with the reaction vessel (A) and outside the furnace were made to have the smallest practicable volume which was small compared to the volume of the vessel. A conventional vacuum system was used consisting of liquid nitrogen cold trap, low pressure gauges, mercury diffusion pump, and rotary fore-pump. This system gave a pressure of less than 10^{-4} mm. mercury.

The oxygen was obtained from a cylinder. It was stored in a large bulb D, dried by phosphorus pentoxide in E, and transferred to the reaction vessel by a simple pump C_1.

The carbon monoxide was prepared by reduction of carbon dioxide with hot zinc (1, 3). The dioxide was generated by heating a dry mixture of sodium carbonate and lead chloride (7) in a tube placed at F. A sample of this gas was isolated and retained for mass spectrometry. The remainder was allowed to circulate by convection through the tube G which contained glass beads covered with zinc dust and heated to 400°C. by an electric furnace. To test for completion of reduction the contents of G and H could be drawn repeatedly through a liquid nitrogen cold trap L by raising and lowering the mercury in K. Reduction was usually allowed to continue overnight by which time no visible amount of dioxide could be condensed in L. Nevertheless the condensable contents of L, if any, were rejected; this ensured that the monoxide was free from dioxide and from moisture. The monoxide was stored in G and H and transferred to the reaction vessel by the pump C_2.

The procedure for making a run was briefly as follows. Measured pressures of the two gases were introduced into A at room temperature. The furnace was then heated at the desired rate and the temperature and pressure were noted at frequent intervals. A graph of pressure against temperature then showed initially the ordinary gas expansion but as reaction commenced the pressure dropped more or less rapidly according to conditions. Explosions in the reaction vessel were detected by a sharp 'kick' of the manometer followed by an instantaneous drop in pressure. After the reaction was completed the system was allowed to cool to room temperature and the pressure measured. The over-all decrease in pressure gave the measure of the extent of the reaction. In most runs the initial pressures (cold) of monoxide and oxygen would be approximately 10 cm. mercury and 2 cm. mercury respectively. A large proportion of the oxygen would be burned (see Table I for details). When pressure measurements were complete the carbon dioxide produced by the reaction was collected in the sampling bulb at B.

The condition which apparently produced the slow or heterogeneous reaction was to heat the reactants at about 550°C. At this temperature the reaction as followed by the pressure–temperature graph proceeded fairly rapidly and was complete, in so far as the proportions of gases allowed, in about an hour.

The condition required to produce an explosion (by heat) was to heat the mixture as rapidly as possible. At about 600°C. which was reached in about eight minutes in this apparatus, the explosion occurred and the furnace was immediately shut off. It is obvious that a certain amount of slow reaction must occur before the explosion takes place and it was observed that if the mixture was heated slowly then the initial slow reaction would proceed so far that no explosion was possible even at temperatures above that normally required to cause explosion.

In a few experiments the carbon monoxide, about 10 cm. mercury pressure, was heated at 700°C. and then a small quantity of oxygen admitted and the furnace shut off. The amount of oxygen admitted was determined by previous calibration experiments.

Experiments on sparking of mixtures were made by using a glass reaction vessel with tungsten wire electrodes across which a spark could be made by applying a high voltage coil. This vessel was filled with gas mixture by attachment to the main apparatus but the pressure of the gas before and after sparking was measured in an auxiliary system equipped with mercury manometer and a simple arrangement for transferring the carbon dioxide produced by the explosion to a sampling bulb.

The carbon dioxide samples so obtained were transferred to another vacuum line where the following operations could be performed by conventional techniques. In the first place the samples were equilibrated with water by being shaken overnight with a few milliliters of water in a sealed bulb. This is to ensure that all carbon dioxide samples have the same O^{16}, O^{17}, O^{18} content; a special stock of water was retained for this purpose. Secondly the samples were dried over magnesium perchlorate. Finally they were transferred to sample tubes designed to fit onto the mass-spectrometer sampling system.

MASS SPECTROMETRY

The carbon dioxide samples were analyzed with a 6-in. radius, 90° deflection mass spectrometer similar to one described by Graham, Harkness, and Thode (5). Mass spectra were obtained by magnetic scanning and were recorded with a Leeds and Northrup type G Speedomax. For each sample, 20 to 30 spectrograms were recorded by scanning alternately from mass 44 to 46 and then in the reverse direction from mass 46 to 44. The resolution of the mass spectrometer was such that the ion peaks were completely resolved. Possible systematic errors arising from mass discrimination and nonlinearity of the amplifying and recording systems were negligible.

Because isotopic abundance ratios, as determined by the mass spectrometer, show small variations from day to day, each sample of carbon dioxide prepared by the combustion of the monoxide was compared mass spectrometrically with a standard sample of carbon dioxide. For the inactive samples the standard was prepared from normal sodium carbonate, and for the active samples from sodium carbonate containing about one per cent C^{14}, as described above. The peak height ratios (45)/(44) and (46)/(44) obtained for each sample were normalized by comparison of the corresponding ratios of the accompanying

standard with the average values of these ratios determined from all measurements on the standard.

From the normalized values of the peak height ratios, the C^{13}/C^{12} and C^{14}/C^{12} abundance ratios may be calculated as follows:

$$\frac{(45)}{(44)} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}} = \frac{C^{13}}{C^{12}} + \frac{O^{16}O^{17}}{O^{16}O^{16}}.$$

Therefore,

$$\frac{C^{13}}{C^{12}} = \frac{(45)}{(44)} - \frac{O^{16}O^{17}}{O^{16}O^{16}}. \qquad [1]$$

Similarly

$$\frac{(46)}{(44)} = \frac{C^{14}O^{16}O^{16} + C^{13}O^{16}O^{17} + C^{12}O^{16}O^{18} + C^{12}O^{17}O^{17}}{C^{12}O^{16}O^{16}}$$

$$= \frac{C^{14}}{C^{12}} + \frac{C^{13}}{C^{12}}\cdot\frac{O^{16}O^{17}}{O^{16}O^{16}} + \frac{O^{16}O^{18}}{O^{16}O^{16}} + \frac{O^{17}O^{17}}{O^{16}O^{16}}.$$

Therefore

$$\frac{C^{14}}{C^{12}} = \frac{(46)}{(44)} - \frac{C^{13}}{C^{12}}\cdot\frac{O^{16}O^{17}}{O^{16}O^{16}} - \frac{O^{16}O^{18}}{O^{16}O^{16}} - \frac{O^{17}O^{17}}{O^{16}O^{16}}. \qquad [2]$$

Because all of the carbon dioxide samples and standards were equilibrated with water taken from the same source (a stock of distilled Ottawa River water), their oxygen isotopic ratios were constant. For carbon dioxide gas in equilibrium with Ottawa River water, the ratios ($O^{16}O^{17}/O^{16}O^{16}$), ($O^{16}O^{18}/O^{16}O^{16}$), and ($O^{17}O^{17}/O^{16}O^{16}$) were determined to be 0.000802, 0.004250, and 0.00000016 respectively. The latter ratio is so small that it was neglected in calculating the C^{14}/C^{12} ratio. Equations [1] and [2] may then be expressed as follows:

$$\frac{C^{13}}{C^{12}} = \frac{(45)}{(44)} - 0.000802, \qquad [3]$$

and

$$\frac{C^{14}}{C^{12}} = \frac{(46)}{(44)} - 0.000802\,\frac{C^{13}}{C^{12}} - 0.004250. \qquad [4]$$

In order to be able to measure the isotope effect by the present method it is necessary that no significant exchange take place between the carbon dioxide produced and the unreacted monoxide under the conditions of the reactions. This was studied in the following manner. The furnace was filled with radioactive carbon monoxide (5.70 cm. mercury) and ordinary inactive carbon dioxide (4.20 cm. mercury). The mixture was heated at 610–630°C. for an hour and then cooled. The dioxide was removed and transferred to a bulb containing 1.5 ml. $N/5$ sodium hydroxide solution. The sodium carbonate solution thus obtained was diluted to 10 ml. and aliquots were counted in a methane filled proportional counter of known efficiency (52%). Knowing the C^{14} content of the initial monoxide and the specific activity of the final dioxide it was calculated that not more than one per cent exchange had occurred. This is not sufficient to cause any trouble in measuring the isotope effect.

RESULTS

Reaction Data

The data for the various runs are summarized in Table I. The table shows the initial pressure of carbon monoxide and oxygen, the temperature conditions, the percentage of the monoxide burned, and whether or not an explosion occurred. It is assumed that for run No. 14 where oxygen was admitted to carbon monoxide preheated at 700° C. an explosion would have occurred; the characteristic 'kick' of the manometer was not observable owing to the abrupt change in pressure caused by admitting the oxygen.

TABLE I
SUMMARY OF REACTION DATA

Run No.	Cm. mercury p, CO	Cm. mercury p, O_2	Conditions	CO reacted (%)
Heterogeneous reaction				
12	11.37	2.30	Heat to 700° at ∽20°/min.; maintain five minutes; cool	31.3 ± 1.0
13	10.25	2.10	Heat to 600° at ∽20°/min.; maintain one hour; cool	36.5 ± 1.0
18	10.40	2.00	Heat to 550° at ∽20°/min.; maintain one hour; cool	34.5 ± 1.0
19	10.50	1.85	Heat to 560° at ∽50°/min.; maintain one hour; cool	24.7 ± 1.0
Homogeneous (explosive) reaction				
14	19.95	3.95	Admit oxygen to monoxide preheated at 700°; cool	39.7 ± 4.0
15	20.50	4.00	Sparked	61.5
16	21.95	2.15	Sparked	31.0 ± 1.0
17	20.30	3.05	Sparked	28.1 ± 1.0
20	10.30	2.05	Heat to 700° at ∽70°/min.; cool (explosion occurred at 580°)	27.0 ± 1.0
22	10.50	1.90	Heat to 630° at ∽100°/min.; cool (explosion occurred at 575°)	32.9 ± 1.0

Notes: (*1*) *In run 15 the percentage reaction was uncertain; this is of no consequence since there was no isotope effect for this run.*
(*2*) *If an explosion was observed the reaction is classified as "homogeneous". Where no explosion occurred the reaction is classified as "heterogeneous".*

Mass Spectrometer Analyses

Table II gives a summary of the mass spectrometer data. *Because the standard was a sample of the carbon dioxide from which the monoxide was prepared, it had the same C^{12}:C^{13}:C^{14} content as the monoxide used in all reactions.* The standard was mass-analyzed each time a sample was analyzed. The average values of the (45)/(44) and (46)/(44) ratios obtained from all the measurements on the standard were 0.01200 and 0.01560 respectively, corresponding to C^{13}/C^{12} and C^{14}/C^{12} ratios of 0.01120 and 0.01134 respectively. Over a period of three months, the day-to-day variations in the standard ratios were small, the maximum deviation from the mean being 0.5%. The average values

of the standard ratios were used in the normalization of the sample peak height ratios. Table II shows the *normalized* values of peak height ratios, (45)/(44) and (46)/(44), for each of the samples, and also the corresponding values of the isotopic abundance ratios, C^{13}/C^{12} and C^{14}/C^{12}, calculated as explained in the experimental section above.

TABLE II

SUMMARY OF MASS SPECTROMETER DATA (NORMALIZED)

Average values for the standard used in normalizing sample values:*

$$\frac{(45)}{(44)} = 0.01200; \quad \frac{C^{13}}{C^{12}} = 0.01120$$

$$\frac{(46)}{(44)} = 0.01560; \quad \frac{C^{14}}{C^{12}} = 0.01134$$

Run	$\frac{(45)}{(44)}$	$\frac{(46)}{(44)}$	$\frac{C^{13}}{C^{12}}$	$\frac{C^{14}}{C^{12}}$
Heterogeneous reaction				
12	.01186		.01106	
13	.01186		.01106	
18	.01185	.01524	.01105	.01098
19	.01185	.01517	.01105	.01091
Homogeneous (explosive) reaction				
14	.01199		.01119	
15	.01199		.01119	
16	.01202	.01559	.01122	.01133
17	.01198	.01555	.01118	.01129
20	.01203	.01555	.01123	.01129
22	.01204	.01558	.01124	.01132

**The C^{13} ratios for the natural monoxide (runs 12–15) and the monoxide containing C^{14} (runs 16–22) were almost identical, and thus both sets of results have been normalized to the same value.*

Ratio of Rate Constants

Because of the low concentration of $C^{13}O$ (or $C^{14}O$) in the monoxide the reaction will be first order in respect to these species (even though it may not be first order in respect to carbon monoxide). The ratios of the rates of reactions k^{13}/k^{12} and k^{14}/k^{12} were calculated on this assumption and are shown in Table III. The errors quoted are based on the standard deviation of the mass spectrograms. Errors in measuring the extents of the reactions are not important.

TABLE III

RATIOS OF RATE CONSTANTS

Run	k^{13}/k^{12}	k^{14}/k^{12}
Heterogeneous reaction		
12	$0.985_0 \pm 0.002$	
13	$0.984_2 \pm 0.002$	
18	$0.983_6 \pm 0.004$	$0.961_0 \pm 0.006$
19	$0.984_6 \pm 0.002$	$0.956_2 \pm 0.004$
Homogeneous (explosive) reaction		
14	$0.998_4 \pm 0.003$	
15	$0.998_4 \pm 0.002$	
16	$1.002_2 \pm 0.003$	$0.998_4 \pm 0.003$
17	$0.998_0 \pm 0.003$	$0.995_0 \pm 0.005$
20	$1.002_0 \pm 0.004$	$0.994_3 \pm 0.005$
22	$1.004_3 \pm 0.004$	$0.994_4 \pm 0.006$

DISCUSSION OF RESULTS

The outstanding feature of the results is that the homogeneous "explosive" reactions (Runs 14, 15, 16, 17, 20, 22) show no isotope effect whereas the heterogeneous "slow" reactions produce a small but distinct effect, the heavier molecules reacting more slowly. The distinction between the two mechanisms is thus nicely emphasized.

Heterogeneous Reactions

The four observed values for k^{13}/k^{12} are 0.985, 0.984, 0.984, and 0.985. The two observed values of k^{14}/k^{12} are 0.961 and 0.956. Since these apply to heterogeneous reactions it is an obvious step to interpret these ratios in terms of the number of collisions made by $C^{12}O$, $C^{13}O$, and $C^{14}O$ molecules with the walls of the vessel. It is most interesting to carry out this interpretation in terms of Eyring's theory of rate processes because this approach is the one which has been used with some success in the interpretation of isotope effects in general.

According to Eyring (4) the activated complex for an adsorption process in which the adsorbed layer is mobile may be considered as the gas molecule just before it strikes the surface. In this case the vibrational and rotational partition functions of the reactant and of the activated complex are the same. On the other hand the reactant has three degrees of translational motion whilst the activated complex has only two so that the ratio of the partition functions of the complex to those of the reactant reduces to

$$\frac{2\pi m\ k\ T/h^2}{(2\pi m\ k\ T)^{3/2}/h^3} = \frac{h}{(2\pi m\ k\ T)^{1/2}}.$$

The rate of adsorption, v, thus becomes

$$v = C_g \frac{kT}{h} \cdot \frac{h}{(2\pi\ m\ k\ T)^{\frac{1}{2}}} e^{-\epsilon/kT}$$

where C_g is the concentration of reactant in the gas, ϵ is the zero point energy of the molecule, and the other symbols have their usual meaning.

The ratio of the rates of adsorption for two isotopically distinguished molecules m_1 and m_2 will be

$$\frac{v_1}{v_2} = \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} e^{-(\epsilon_1-\epsilon_2)/kT}.$$

This will give the ratio of the rates of reaction provided adsorption is the rate controlling step and the adsorbed layer is mobile. Since $(\epsilon_1 - \epsilon_2)$ is a small quantity and T is large, 900° Kelvin in the present experiments, this expression leads to the conclusion that the rates of reaction should be inversely proportional to the square roots of the mass of the molecules. In this case k^{13}/k^{12} should be $\sqrt{28/29} = 0.983$ and k^{14}/k^{12} should be $\sqrt{28/30} = 0.966$. The agreement with experiment in the case of k^{13}/k^{12} is very good and in the case of k^{14}/k^{12} is reasonable considering the experimental errors. The same conclusion could of course have been reached by considering the classical collision frequencies of the various molecules with the walls of the vessel and neglecting any differences in the energy of activation of adsorption.

Homogeneous Reactions

An accepted mechanism for the reaction (6) involves the following chain propagating and branching steps:

$$CO + O_3 = CO_2 + O + O,$$
$$O + O_2 = O_3.$$

The activated complex for the reaction can in this case be represented as

$$O—C \ldots O—M$$

where M is O_2 treated as a point mass. If it is assumed that this complex is linear, which is reasonable, the vibration frequencies may be readily calculated for any given set of masses and potential constants. The isotope effect can then be obtained using Bigeleisen's formula (see Ref. 2 where the derivation and significance of this equation is described)

$$\frac{k_1}{k_2} = \frac{K_1}{K_2}\left(\frac{\nu_{1L}}{\nu_{2L}}\right)\left[1 + \sum_i G(u_i)\Delta u_i - \sum_i G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right].$$

In using this formula it is necessary to neglect the effect of mass on transmission coefficients K_1/K_2. At the temperatures of the present reactions the "free energy" term $(1 + \sum_i G(u_i)\,\Delta u_i - \sum_i G(u_i^{\ddagger})\,\Delta u_i^{\ddagger})$ is effectively unity. Using the proposed model it can also be shown that the ratio of the frequencies along the reaction co-ordinate ν_{1L}/ν_{2L} is also very close to unity for a wide range of potential constants and M = O_2 (i.e. O_3 as reactant). It is also very close to unity if M is taken as a "third body" with no O—M bond but having a weak repulsion between M and the carbon atom.

It follows that, assuming the ratio of transmission coefficients to be unity, there will be no isotope effect, in agreement with the experimental results.

It is interesting to look briefly at the situation from the point of view of simple collision theory, i.e. using the expression:

$$\frac{k_1}{k_2} = \frac{P_1 Z_1}{P_2 Z_2} e^{-\Delta E/RT}$$

where ΔE is the difference in experimental activation energies for the isotopic molecules. Since ΔE is presumably small and T is large the term $e^{-\Delta E/RT}$ should be close to unity. On the other hand the term Z_1/Z_2 (ratio of collision frequencies) is not unity. Table IV shows the value of Z_1/Z_2 for $C^{13}O$ compared to $C^{12}O$ and for $C^{14}O$ compared to $C^{12}O$ assuming in one case (column 1) that the collisions occur between carbon monoxide and oxygen atoms and in the other case (column 2) between monoxide and ozone molecules.

TABLE IV
RATIOS OF COLLISION FREQUENCIES

	O	O_3
$C^{13}O/C^{12}O$	0.9937	0.9891
$C^{14}O/C^{12}O$	0.9878	0.9787

Comparison of Tables IV and III shows differences which are probably significant, i.e. the ratios of rate constants expected on the basis of collision numbers only is not in agreement with the measured values. Part or even all of this discrepancy could be accounted for by allowing that the term $e^{-\Delta E/RT}$ is not unity, ΔE being negative in just the amount required to compensate for the Z_1/Z_2 term. Unfortunately there is no simple way of estimating ΔE. Furthermore there is no knowledge of the effect of isotope substitution on the factor P. For these reasons the simple collision theory is of little use in considering isotope effects.

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GLUTAMIC ACID AS AN ADDITION AGENT IN THE ELECTRODEPOSITION OF COPPER[1]

By S. Adamek and C. A. Winkler

ABSTRACT

The polarization–time curves obtained in the presence of glutamic acid generally showed two distinct polarization levels, one corresponding to an induction period following an initial rapid increase of polarization from the standard surface value, and the other corresponding to a steady state period following a second rapid increase of polarization. The polarization at both levels increased with increase of glutamic acid concentration and decreased with increase of sulphuric acid concentration in the electrolyte. In general, the induction period increased, and eventually became irreproducible, with increased sulphuric acid and copper sulphate concentrations, decreased glutamic acid concentration, decreased current density, increased temperature, and addition of chloride. Addition of sufficient chloride prolonged the induction period indefinitely at a polarization level corresponding to the presence of chloride alone. Following the induction period, the concentration polarization increased with glutamic acid concentration and was considerably higher than the value obtained during the induction period. Addition of chloride decreased the concentration polarization.

INTRODUCTION

Several previous papers from this laboratory have discussed the changes in cathode polarization during the deposition of copper when gelatin alone, or gelatin plus chloride ion, are present as addition agents in the electrolyte (5, 6, 12, 14). The increase in polarization observed in the presence of gelatin alone has been interpreted as a consequence of an increase in true current density when the active area of the cathode is reduced by adsorption of gelatin. A marked decrease in polarization below the value observed with gelatin alone, when small quantities of chloride ion (of the order 2 mgm. per liter) are added with the gelatin, was attributed to an increase of active area by attack of the halide ion on less active parts of the cathode surface.

A recent study of the initial changes in cathode polarization (13) has shown that, in the presence of gelatin but not in its absence, these changes were dependent upon the time the cathode was in contact with the electrolyte before electrolysis was begun. There was just a suggestion from this behavior that corrosion processes, with accompanying formation and adsorption of copper–gelatin complexes, might play a significant part in the addition agent effect of gelatin. Other workers have concluded that substances which function as addition agents form complexes with metal ions in the solution (3, 4, 7–9, 11).

To obtain further information about the way in which complex formation might be concerned in the mechanism of addition agent action, it seemed reasonable to study the behavior of a simple amino acid, rather than gelatin, as the addition agent. The ability of many such acids to form heavy metal complexes is well recognized, and copper complexes with several of them have been isolated. It was also hoped that further study of the effect of chloride ion,

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with the simpler addition agent, might enable a better understanding of the way in which chloride ion exerted its profound effect on the cathode polarization.

Although experiments were made with several amino acids, the increases of polarization appeared to be more pronounced with glutamic than with the other acids used. Hence, it is with glutamic acid that the present paper is primarily concerned.

EXPERIMENTAL AND RESULTS

All polarization measurements were made in a modified Haring cell of the type described previously (12). The auxiliary equipment and procedure for making the measurements have been indicated in several of the earlier papers. The volume of electrolyte used was always 150 ml.

The chemicals used in preparation of the electrolytes were Merck reagent grade copper sulphate pentahydrate, Baker's analyzed C. P. sulphuric acid, reagent grade sodium halides and amino acids, and laboratory distilled water that was redistilled from alkali. Before they were used all electrolytes were brought to the temperature of the thermostat (25 ± 0.1°C.).

Prior to an experiment, the cathode was polished with emery cloth, etched in 1:1 concentrated nitric acid – water solution, and thoroughly washed with distilled water. The surface was then brought to a standard condition by electrodeposition at 25°C. from an electrolyte containing 125 gm. copper sulphate pentahydrate and 90 gm. concentrated sulphuric acid per liter of solution. The deposition was continued for 30 min. at 3 amp./dm.^{2}, then for one hour at 2 amp./dm^2. The polarization at the end of the surfacing procedure was 105 ± 5 mv.

In the presence of glutamic acid, in an electrolyte containing 125 gm./liter copper sulphate pentahydrate and 180 gm./liter sulphuric acid, the polarization generally increased rapidly (within two minutes) to a relatively constant value, (cf. Fig. 1*A*, 1*B*) where it remained for a time which, for brevity, may be referred to as the induction period. Following this induction period, there was observed a second rapid increase to a steady state value which, for given conditions of electrolysis, was reproducible within ± 7 mv. The length of the induction period, on the other hand, was generally quite irreproducible with this electrolyte. Occasionally, families of curves were obtained that showed definite trends of polarization with change of addition agent concentration, especially if the same stock electrolyte were used throughout a given series of experiments. However, use of the same stock electrolyte was no guarantee that reproducibility would be realized. The reproducibility remained poor with different batches of copper sulphate, sulphuric acid, or glutamic acid, and with differently prepared batches of distilled water. A decrease in the sulphuric acid content of the electrolyte (Fig. 1*A*) increased the polarization at both the steady state and induction period levels, and improved the reproducibility considerably. With several different batches of electrolyte containing 200 mgm./liter glutamic acid and 90 gm./liter sulphuric acid, an extreme variation in the induction period from 4 to 10 min. was observed, whereas with electro-

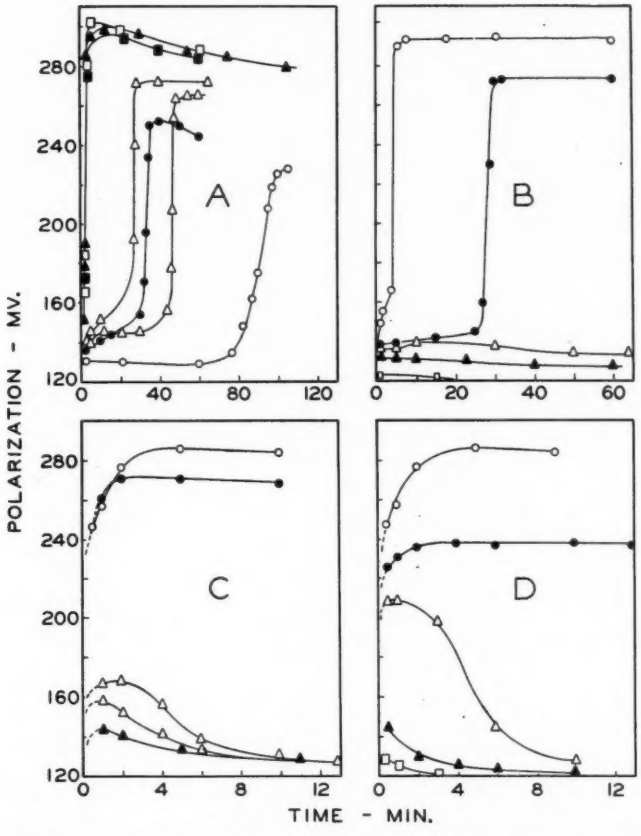

FIG. 1. Effect of various factors on cathode polarization in the presence of glutamic acid.
A. Effect of sulphuric acid concentration. H_2SO_4 conc. (gm./liter): ○ 180; ● 150; △120; ▲ 90; □ 50; ■ 35.
B. Effect of chloride concentration. H_2SO_4 conc., 90 gm./liter. Chloride conc. (mgm./liter): ○ nil; ● 0.145; △0.165; ▲ 0.33; □ 4.
C. Effect of immersion time (cathode surface first subjected to maximum polarization). H_2SO_4 conc., 90 gm./liter. Immersion time (min.): ○ nil; ● 0.5; △ 1.0; ▲ 5.0.
D. Effect of chloride concentration (cathode surface first subjected to maximum polarization). H_2SO_4 conc., 90 gm./liter. Chloride conc. (mgm./liter): ○ 0.5; ● 1.0; △ 1.5; ▲ 2.0; □ 8.0.

lyte containing 180 gm./liter sulphuric acid the variation in induction period was often 10-fold or more, for given conditions of electrolysis. When the sulphuric acid concentration was varied at a low glutamic acid concentration (4 mgm./liter), the induction period again increased with increase of sulphuric acid concentration, but irreproducibility was quite evident at acid concentrations as low as 90 gm./liter.

At a reduced current density of 1 amp./dm.^{2}, a very pronounced increase in induction period (from about 5 min. to 100 min.) resulted when the sulphuric acid concentration was increased from 35 gm./liter to 90 gm./liter.

The effect of glutamic acid concentration on the cathode polarization was determined with an electrolyte containing 90 gm./liter sulphuric acid. (Unless otherwise stated, the electrolyte used in all subsequent experiments contained 125 gm./liter copper sulphate pentahydrate and 90 gm./liter concentrated sulphuric acid). For glutamic acid concentrations above 50 mgm./liter, the induction period varied only slightly, but for smaller concentrations of glutamic acid, it increased considerably as the glutamic acid concentration was decreased, and eventually, for concentrations of glutamic acid below about 5 mgm./liter, erratic induction periods were again observed. Similar trends were noted in electrolytes containing 180 gm./liter sulphuric acid when, by chance, systematic behavior was observed in this more strongly acid solution. Erratic induction periods were not accompanied by erratic behavior of the steady state polarization, as indicated by the relation between the steady state polarization and glutamic acid concentration shown in Fig. 2*A*. In this figure are plotted also

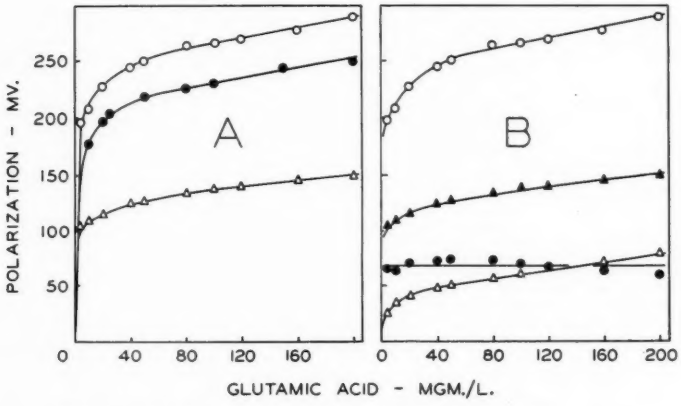

FIG. 2. Effect of glutamic acid on cathode polarization.
A. ○ Steady state polarization. H_2SO_4, 90 gm./liter.
● Steady state polarization. H_2SO_4, 180 gm./liter.
△ Polarization after one minute. H_2SO_4, 90 gm./liter.
B. H_2SO_4, 90 gm./liter.
○ P_T (total steady state polarization in presence of glutamic acid).
△ P_C (concentration polarization following induction period).
▲ P_A (total polarization during induction period).
● $P_T - (P_C + P_A)$.

the polarization values after one minute, corresponding roughly to the polarization at the induction period plateau. The increase in its value with increased glutamic acid concentration is evident. The data of Fig. 2*A* can be well represented as linear relations between the logarithm of the cathode polarization and logarithm of the glutamic acid concentration.

With 200 mgm./liter glutamic acid in the electrolyte, the induction period appeared to increase with a decrease of current density and to become erratic at low current densities, as shown by the following results:

Current density (amp./dm.²)	Induction period (min.)	Steady state polarization (mv.)
3.0	2	330
2.0	4	295
1.5	8	268
1.3	17	240
1.2	26, 60	240, 228
1.1	20	238
1.0	95	234

A decrease in copper sulphate concentration was found to decrease the induction period and increase the polarization in an electrolyte containing 200 mgm./liter glutamic acid. The results were as follows:

Copper sulphate conc. $CuSO_4 \cdot 5H_2O$ (gm./liter)	Induction period (min.)	Steady state polarization (mv.)
Current density = 1 amp./dm.²		
40	<1	330
80	4	244
125	90	234
Current density = 2 amp./dm.²		
125	4	295
190	12	256

The effect of temperature on the polarization behavior at 2 amp./dm.² in the presence of 200 mgm./liter glutamic acid was examined at 19°, 25°, 30°, and 36°C. Without presenting the results in detail, it might be mentioned that increase of temperature decreased the polarization from 320 mv. to 205 mv., and increased the induction period from 5 min. to 60 min., over the range studied. The most marked changes in both quantities appeared to be in the interval 30°–35°C.

Experiments were made to determine whether the second increase in polarization observed in the presence of glutamic acid might be the result of some product formed at the anode and carried to the cathode by convection. One milliliter of glutamic acid solution was added carefully from a pipette, at the base of the anode, while an electrolysis was in progress in the absence of addition agent. Approximately one hour elapsed before any increase of cathode polarization was observed. Repetition of the experiments with gelatin solution instead of glutamic acid solution gave a similar result. Since the induction periods observed in the polarization–time curves discussed previously were frequently much less than one hour for similar conditions of electrolysis, the second increase in polarization apparently is not due to formation of anodic products and their subsequent action at the cathode.

Although it seemed rather unlikely, there was a possibility that the induction period bore some relation to the time required for the acidity of the cathode film to attain a steady concentration. The drainage method described by Brenner (1) was used, and experiments were made at 0.5, 1.0, and 2.0 amp./dm.² in electrolyte containing 90 gm./liter sulphuric acid, and at 2.0 amp./dm.² in electrolyte containing 180 gm./liter sulphuric acid. Since a relatively steady acid concentration in the film was attained in less than two minutes, there

appears to be no relation between this time and the induction period observed in the polarization–time curves. In agreement with Brenner, the acid concentration in the film increased with increase of current density; the percentage increase was approximately the same at the two bulk electrolyte acid concentrations used.

The effect of chloride ion on the cathode polarization in the presence of glutamic acid was studied over a range of conditions. Typical behavior is illustrated in Fig. 1*B*. With addition of chloride in concentrations less than about 0.2 mgm./liter, the induction period with 2 amp./dm.^{2} was increased, but the second increase of polarization did occur to somewhat lower steady state values than in the absence of chloride. With chloride concentrations greater than about 0.2 mgm./liter, however, the induction period appeared to be prolonged indefinitely, and with chloride concentrations of 4 and 8 mgm./liter, and 200 mgm./liter glutamic acid, the polarization followed closely the values in the presence of chloride alone.

When sufficient chloride (6 mgm.) was added at the base of the cathode after the polarization had reached the steady state value in electrolyte containing glutamic acid alone, the polarization began to decrease immediately and rapidly. At the end of 10 min., in a typical experiment, it had decreased some 45 mv., and after 40 min. had fallen to the value characteristic of chloride alone in the electrolyte.

The very high sensitivity of the system to the presence of chloride ion suggested the possibility that the induction period was due to the presence of an impurity (particularly chloride ion) and that the end of the induction period represented depletion of this depolarizer. However, prolonged electrolysis (up to 1½ hr.) at 2 amp./dm.^{2} failed to attain the second increase of polarization when 0.16 mgm./liter chloride was present; with increase of the current density to 3 amp./dm.^{2} the increase of polarization occurred after 10 min. When a fresh cathode was inserted and the current density restored to 2 amp./dm.^{2} the normal induction period was again observed. This type of behavior, which was observed several times, does not indicate consumption of a depolarizer during the induction period.

It is interesting to note that the second increase of polarization could be promoted readily at 3 amp./dm.^{2} with 0.16 mgm./liter chloride, but required 4 amp./dm.^{2} when 0.3 mgm./liter chloride was present. Also, if the higher polarization were induced by a higher current density in the presence of 0.3 mgm./liter chloride, it could also be attained when the current density was restored to 2 amp./dm.^{2} provided current flow was not interrupted. With 0.16 mgm./liter chloride, similar procedure allowed the second polarization increase to occur at the lower current density even after short periods of current interruption.

The behavior summarized briefly above apparently had no relation to the surface condition of the cathode. Cathodes were prepared with quite different surface grain sizes, by polishing and etching and by deposition at current densities of 1.0, 2.0, and 3.0 amp./dm^2. There were no significant differences in the polarization–time curves with the different cathodes in an electrolyte

containing 200 mgm./liter glutamic acid and with a current density of 2 amp./dm^2.

The effect of chloride on the polarization was investigated further with cathodes that were given the usual standard surface, after which they were subjected to deposition from electrolyte containing glutamic acid (200 mgm./liter) until the polarization had attained its maximum value. The cathode was then transferred to fresh electrolyte containing both glutamic acid and chloride, where it was allowed to remain for various immersion times before current flow was begun. The results for several immersion times at given chloride concentration, and for several chloride concentrations at zero immersion time, are shown in Figs. 1*C* and 1*D*. The behavior, in general, suggests two competitive processes, one of which tends to increase, the other to decrease the polarization.

The effect of halides, other than chloride, on the polarization in the presence of glutamic acid was also studied, but the results will not be presented in detail. It suffices to mention that fluoride ion had no effect whatever, which is reminiscent of its behavior when gelatin was the addition agent (12), whereas both bromide and iodide ions reduced the polarization in a manner similar to chloride, although with less effectiveness. With iodide, the decrease in polarization was followed by an increase as electrolysis was continued.

The change in concentration polarization brought about by the presence of glutamic acid in the electrolyte was estimated by the method outlined in a previous paper (13). Briefly, it consisted of measuring with a calibrated oscilloscope the extent of relatively slow polarization decay when current flow through the Haring cell was interrupted.

When the polarization in the presence of glutamic acid was allowed to attain its maximum value before electrolysis was stopped, the concentration polarization was linearly related to the glutamic acid concentration:

Glutamic acid conc. (mgm./liter)	Concentration polarization (mv.)
0	20
40	28
100	40
200	60

On the other hand, decrease of the copper sulphate concentration from 125 gm./liter to 60 gm./liter, or the sulphuric acid concentration from 90 gm./liter to 45 gm./liter, in the presence of 200 mgm./liter glutamic acid, had no effect on the concentration polarization.

Concentration polarization during the induction period in electrolyte containing 200 mgm./liter glutamic acid was approximately 30 mv.

Addition of a small amount of chloride (e.g. 1 mgm.), with 200 mgm./liter glutamic acid resulted in a decrease of concentration polarization to values comparable with the value obtained in the absence of addition agent.

It is of particular interest to note that the quantity $P_T - (P_C + P_A)$ is essentially constant, where

P_T = Total steady state polarization in the presence of glutamic acid.
P_C = Concentration polarization following the induction period.[2]
P_A = Total polarization during the induction period.

The behavior is illustrated in Fig. 2*B*. Extrapolated values of the concentration polarization were used for glutamic acid concentrations below 40 mgm./liter.

The changes in polarization brought about by several compounds related to glutamic acid were studied in an electrolyte containing 125 gm./liter copper sulphate, 90 gm./liter sulphuric acid, and 200 mgm./liter of the addition agent. The compounds studied were glycine, α-amino-*n*-butyric acid, α-amino-*n*-valeric acid, serine, β-phenylalinine, leucine, valeric acid, glutaric acid, and aspartic acid. Briefly summarized, the results indicated that mono-amino dicarboxylic acids (aspartic and glutamic) are much more effective as addition agents than the mono-amino monocarboxylic acids. Also, it would appear that in an homologous series of amino acids of increasing chain length (glycine, α-amino butyric, α-amino valeric, and also aspartic and glutamic), the effectiveness as an addition agent increased with chain length. Glycine and α-amino butyric had relatively little effect on the polarization and failed to produce the second increase in polarization that was characteristic of the other amino acids studied. Valeric and glutaric acids were without effect on the polarization, serine gave an initial increase (40 mv.) which gradually returned to the standard state value, and β-phenylalinine gave a gradual increase that eventually amounted to about 40 mv.

DISCUSSION

The rapidity of the first increase of polarization in the presence of glutamic acid, together with the relation between the polarization during the induction period and the concentration of glutamic acid (Fig. 2*A*), suggest that adsorption of some species on the active centers of the cathode is responsible for the increase in polarization to the induction period plateau. Since the length of the induction period was found to be independent of the surface for surfaces prepared in the absence of glutamic acid, but not for surfaces prepared in its presence, the indications favor a copper–glutamic complex as the adsorbed species. Further, the complex involved would probably be with cuprous ion[3] if deposition is assumed to occur by a sequence of single electron transfers (2) from the cathode

$$Cu^{++} + e \rightarrow Cu^{+}, \qquad [1]$$

$$Cu^{+} + e \rightarrow Cu, \qquad [2]$$

or by the first of these followed by a chemical change (dismutation) on the surface (10),

$$2\,Cu^{+} \rightarrow Cu + Cu^{++}. \qquad [3]$$

The second increase in polarization following the induction period suggests initiation of a new process corresponding to a higher deposition potential.

[2]*P_C may be regarded as the sum of the concentration polarization (practically independent of glumatic acid concentration) during the induction period and an increment in concentration polarization (dependent upon addition agent concentration) following the induction period.*

[3]*In the absence of oxygen, a light blue color developed in a solution of cuprous chloride to which glutamic acid was added.*

There are several indications that this might be a consequence of cuprous ion depletion adjacent to the cathode face. With passage of current several factors tend to reduce the cuprous ion concentration in the cathode film below the value determined in the absence of current flow by the equilibrium $Cu^{++} + Cu \rightleftarrows 2\,Cu^{+}$. These include increase of current density and decrease of copper sulphate concentration, for obvious reasons, together with decrease of temperature, which operates by reducing the rates of diffusion and convection into the film and by altering the equilibrium constant of reaction (4). These same factors have been found to decrease the induction period during deposition in the presence of glutamic acid. It will also be recalled that the concentration polarization was considerably higher after, than during, the induction period, and that the concentration polarization after the induction period was observed to increase with increase of glutamic acid concentration. This behavior might be expected if cuprous–glutamic complex formation occurred, as suggested previously, with an accompanying decrease in cuprous ion concentration.

While, as indicated by these arguments, the induction period appears to be associated with depletion of cuprous ions, a reasonable explanation has not been found on this basis for the observed large variations in induction period, particularly with change of sulphuric acid concentration. However, attempts to interpret the induction period from other points of view, such as adsorption phenomena, appear to encounter equally formidable difficulties.

Whatever might be its cause, it is suggested that the second increase of polarization initiates the discharge of cuprous–glutamic complexes, at a potential corresponding to the steady state polarization. Accordingly, the steady state polarization (P_T) might be regarded as the sum of:

(*a*) polarization corresponding to the potential level of the induction period (P_A), postulated to involve adsorption of copper–glutamic complexes,

(*b*) concentration polarization (P_C) following the induction period,

(*c*) polarization due to discharge of complexes following the induction period.

The value of (*c*) alone, given by $P_T - (P_C + P_A)$, should then be independent of the glutamic acid concentration. This was indeed found to be essentially true (Fig. 2*B*).

The very small quantities of chloride ion necessary to reduce markedly the polarization in the presence of glutamic acid, together with the high rate with which the polarization is reduced, do not encourage the view expressed in previous papers that chloride exerts its influence through a corrosion type of process. An alternative suggestion is that chloride ion might facilitate electron transfer by acting as an electron "bridge", in the manner suggested by Heyrovsky (10) to account for the accelerated deposition of zinc on a mercury cathode in the presence of chloride ion. In the present system, the electron "bridges" might be assumed to facilitate electron transfer from the cathode to copper–glutamic complexes on the surface or to operate between complexes to promote their decomposition,

$$2\,[\mathrm{Cu-Glutamic}]^{+} \rightarrow \mathrm{Cu}^{++} + \mathrm{Cu} + 2\,[\mathrm{Glutamic}].$$

Failure of the fluoride ion to function in the manner of the other halides to reduce the polarization can be ascribed simply to its relative unpolarizability. Obviously, the decrease in polarization brought about by chloride ion when gelatin is the addition agent, though not the subsequent increase at higher chloride concentrations, might be explained in a similar way, by assuming adsorption of copper–gelatin complexes. It must be emphasized, however, that glutamic acid and gelatin differ considerably in their behavior as addition agents. It is hoped that studies now in progress with other simple compounds which produce addition agent effects more closely simulating those of gelatin will permit stronger convictions about the importance of complex formation in systems containing gelatin.

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PHTHALIDE FORMATION

III. CONDENSATIONS WITH 5-HYDROXY-2-METHYLBENZOIC ACID[1]

By E. H. Charlesworth, E. A. Dudley, E. E. Nishizawa, and W. Radych

ABSTRACT

The product obtained from the condensation of 5-hydroxy-2-methylbenzoic acid with aqueous formaldehyde and hydrochloric acid is dependent on the temperature. If the condensation is carried out at room temperature 3-hydroxy-6-methylphthalide results. This substance can also be obtained by the demethylation of 3-methoxy-6-methylphthalide. If the condensation is carried out at the boiling point the lactone of 8-hydroxymethyl-1,3-benzodioxane-6-methyl-7-carboxylic acid results. Proof of the presence of the *m*-dioxane and phthalide rings in this latter substance has been established by opening these rings in succession. In both cases this has led by a series of degradative steps to 4-methoxybenzene-1,2,3,5-tetracarboxylic acid. The structure of this acid has been confirmed by its synthesis in six unambiguous steps from mesitylene.

INTRODUCTION

When 5-hydroxy-2-methylbenzoic acid (I) is condensed with aqueous formaldehyde and hydrochloric acid at room temperature 3-hydroxy-6-methylphthalide (II) is obtained. However when the condensation is carried out at the boiling point the lactone of 8-hydroxymethyl-1,3-benzodioxane-6-methyl-7-carboxylic acid (III) is produced. The phthalide (II) has also been formed by demethylation with hydriodic acid or aluminum chloride of 3-methoxy-6-methylphthalide (IV) prepared according to the directions of Charlesworth *et al.* (2).

The structure of the dioxanylphthalide (III) has been established from its preparation by further condensation of the phthalide (II) and also by the opening of the *m*-dioxane and phthalide rings in succession, with a study of the degradation products resulting therefrom. When the dioxanylphthalide (III) was oxidized with chromic oxide and acetic acid, the methylene ether – ester (V) was formed. On alkaline hydrolysis of V a molecule of formaldehyde split out and the hydroxy acid (VI) was produced. This could be readily methylated to VII. The free carboxyl groups of either VI or VII could be removed by heating with quinoline and copper chromite to yield the aforementioned phthalides II and IV respectively. By oxidation with alkaline permanganate at 60°C. the phthalide ring of VII was opened and the tricarboxylic acid (VIII) was formed. On more drastic oxidative treatment, the methyl side chain was attacked and the final tetracarboxylic acid (IX) was obtained.

If the dioxanylphthalide (III) was oxidized originally with alkaline permanganate, the dioxane ring is left intact and the phthalide ring was opened to produce the dioxanylphthalic acid (X). This acid readily formed the anhydride (XI) and the imide (XII). The acid (X) on treatment with chromic oxide and

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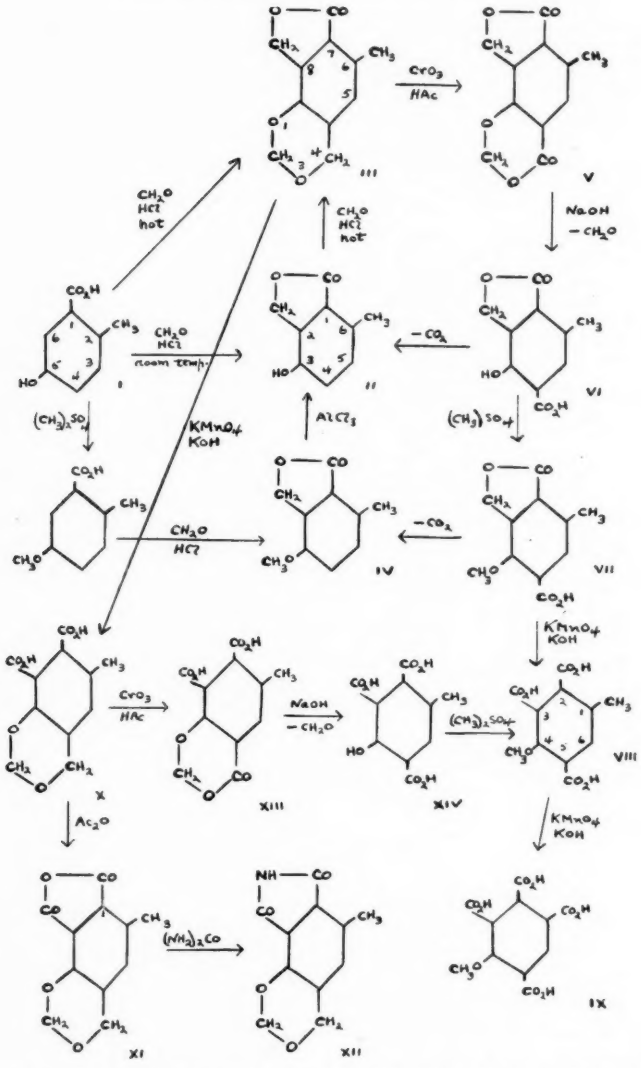
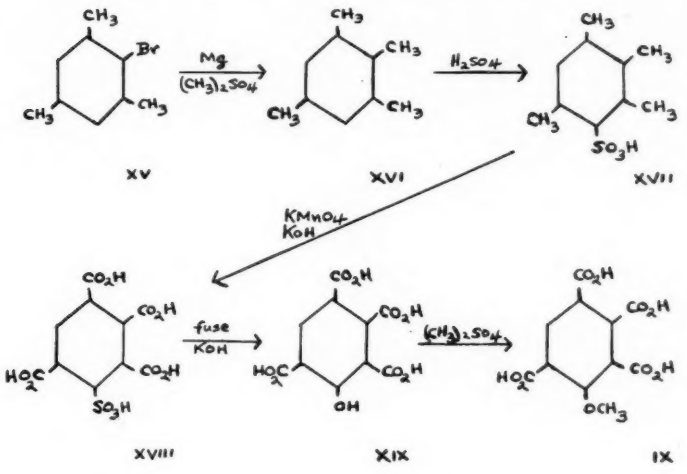
Contribution from the Department of Chemistry, the University of Manitoba, Winnipeg, Man.
For Part II in this series, see Can. J. Chem. 31: 65. 1953.



acetic acid gave the methylene ether – ester (XIII) which on alkaline hydrolysis lost formaldehyde and formed the hydroxytricarboxylic acid (XIV). Methylation of XIV gave the previously obtained acid (VIII).

The structure of the acid (IX) has been confirmed by its synthesis in six unambiguous steps from mesitylene. Bromomesitylene (XV) was methylated by treating its Grignard derivative with methyl sulphate to give isodurene (XVI). The sulphonic acid (XVII) of isodurene was oxidized with alkaline permangante to yield the tetracarboxylic sulphonic acid (XVIII). Fusion with



potash gave the phenolic tetracarboxylic acid (XIX) and methylation 4-methoxybenzene-1,2,3,5-tetracarboxylic acid identical with the degradative acid (IX).

Since the publication of Part II (1) the hydrolysis of the lactone of 6-hydroxymethyl-8-methyl-1,3-benzodioxane-4-one-5-carboxylic acid has been accomplished to yield 5-hydroxy-4-methylphthalide-6-carboxylic acid, m.p. 195°C. This has been reported also in the meantime by Duncanson, Grove, and Zealley (3) in connection with their work on gladiolic acid.

EXPERIMENTAL

Most of the 2-methylbenzoic acid used in this research was prepared by the oxidation of *o*-xylene by dilute nitric acid as described by Zaugg and Rapala (9). 5-Hydroxy-2-methylbenzoic acid (I), 5-methoxy-2-methylbenzoic acid (II), and 3-methoxy-6-methylphthalide (IV) were made as described by Charlesworth *et al.* (2) in the first paper of this series.

3-Hydroxy-6-methylphthalide (II)

This product was formed by the demethylation of the corresponding methoxyphthalide (III). Two methods were employed:

(*a*) A mixture of 3-methoxy-6-methylphthalide (2.0 gm.), hydriodic acid (20 ml., sp. gr. 1.7) and red phosphorus (5.0 gm.) was refluxed gently under an atmosphere of nitrogen for three hours. The solid material was filtered off, washed with water, and dissolved in hot alcohol (charcoal). The hydroxyphthalide was crystallized from the alcohol in fine colorless needles (0.8 gm.) which melted at 223–224°C.

(*b*) A mixture of 3-methoxy-6-methylphthalide (1.1 gm.) and anhydrous aluminum chloride (2.7 gm.) in dry benzene (40 ml.) was refluxed on a water bath for 10 hr. The solid was filtered off, washed with water, and dried. On crystallization from alcohol, needles (0.5 gm.) which melted at 223–224°C.

were obtained. The compound was very soluble in alcohol, acetone, ether, and hot sodium hydroxide solution. It was insoluble in water and 5% sodium bicarbonate solution. On warming this substance with resorcinol and concentrated sulphuric acid followed by sodium hydroxide solution, the greenish fluorescence characteristic of the phthalide ring developed. Found: C, 65.8; H, 4.98%; mol. wt., 168. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%; mol. wt., 164.

The above hydroxyphthalide can also be obtained by allowing a well shaken mixture of 5-hydroxy-2-methylbenzoic acid, formaldehyde solution, and concentrated hydrochloric acid to stand overnight at room temperature. The solid then on top of the liquid layer was filtered off, washed, and crystallized from alcohol. It melted at 223–224°C. with no depression on mixing with the above samples.

If a sample of the hydroxyphthalide was refluxed with formaldehyde solution and concentrated hydrochloric acid it was converted to the dioxanylphthalide (III) m.p. 171–172°C.

The Lactone of 8-Hydroxymethyl-1,3,-benzodioxane-6-methyl-7-carboxylic Acid (III)

A mixture of 5-hydroxy-2-methylbenzoic acid (30 gm.) and formaldehyde solution (300 ml., 40%) was heated in a 2 liter flask over a wire gauze until the acid just dissolved. At this point concentrated hydrochloric acid (300 ml.) was added through the top of the reflux condenser and the mixture was boiled. In the first few minutes of heating after the addition of the hydrochloric acid, a flocculent white precipitate separated, a small sample of which was removed and found to be the above hydroxyphthalide (II) m.p. 223–224°C. As the boiling continued, the flocculent precipitate dissolved and then a second product separated in the form of light brown granules. After a total of one hour's boiling the mixture was cooled and the crude dioxanylphthalide (30 gm.) filtered off. It was dissolved in boiling alcohol (*ca.* 2 liters) and filtered from a little insoluble material. On cooling, the dioxanylphthalide separated as coarse, white needles which melted at 171–172°C. A small sample was recrystallized for analysis from acetone from which it separated in characteristic long needles. Found: C, 64.0; H, 4.91%; mol. wt., 204. Calc. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.89%; mol. wt., 206. It gives the phthalide test with resorcinol and concentrated sulphuric acid. When the sample was warmed with phloroglucinol and strong sulphuric acid a reddish precipitate was formed which Mehta and Ayyar (6) have used to confirm the *m*-dioxane ring.

The Lactone of 8-Hydroxymethyl-6-methyl-1,3-benzodioxane-4-one-7-carboxylic Acid (V)

The dioxanylphthalide (III) (10 gm.) was dissolved in warm glacial acetic acid (250 ml.). The reaction flask was cooled externally with cold water, and finely ground chromium trioxide (15 gm.) was added with stirring at such a rate that the temperature was maintained at 65–70°C. When the reaction appeared to be complete the mixture was diluted with water to a volume of 2 liters and allowed to stand overnight. White, fluffy needles (2.5 gm.) separated which were filtered off, dried, and recrystallized from acetone. The white

needles thus obtained melted at 184–185°C. Found: C, 60.4; H, 3.64%. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.65%.

3-Hydroxy-6-methylphthalide-4-carboxylic Acid (VI)

A mixture of the above methylene ether – ester (V) (5.0 gm.) and sodium hydroxide solution (50 ml., 10%) was refluxed for one hour. A homogeneous solution gradually developed with the evolution of formaldehyde. The reaction mixture was cooled, filtered, and acidified with concentrated hydrochloric acid. The precipitate thus obtained was filtered off and dried. On recrystallization from water the acid was obtained as a white powder (4.0 gm.) which melted at 238°C. and which gave a dark violet color with 1% ferric chloride solution. Found: C, 57.6; H, 3.95%. Calc. for $C_{10}H_8O_5$: C, 57.7, H. 3.87%.

3-Methoxy-6-methylphthalide-4-carboxylic Acid (VII)

The hydroxy compound (VI) (7.5 gm.) was methylated in the usual manner with methyl sulphate and sodium hydroxide solution. After it was boiled with excess sodium hydroxide solution to hydrolyze any methyl ester, the mixture was acidified with hydrochloric acid. The crude acid (7.0 gm.) was twice recrystallized from water, from which it separated in white needles (6.0 gm.); these melted at 150–151°C. and gave no phenolic test with ferric chloride solution. Found: C, 59.6; H, 4.47%; neut. equiv., 218. Calc. for $C_{11}H_{10}O_5$: C, 59.5; H, 4.54%; neut. equiv., 222.

3-Methoxy-6-methylphthalide (IV)

The above 4-carboxylic acid (VII) (1.0 gm.) was decarboxylated by heating at 180°C. for 15 min. with quinoline (15 ml.) and copper chromite (0.01 gm.). The mixture was cooled and poured into 10% hydrochloric acid (150 ml.). The phthalide separated as white needles which were crystallized from alcohol. They melted at 165–166°C. and showed no depression of melting point on being mixed with a sample of the phthalide produced by the method of Charlesworth *et al.* (2) from 5-methoxy-2-methylbenzoic acid.

If a similar decarboxylation with quinoline and copper chromite was carried out on the hydroxy acid (VI), the hydroxyphthalide was obtained, which melted at 223–224°C. and with no depression on being mixed with an authentic sample (II), described earlier in this section.

1-Methyl-4-methoxybenzene-2,3,5-tricarboxylic Acid (VIII)

A solution of the above methoxyphthalide (VII) (3.0 gm.) in 3.5% aqueous potassium hydroxide solution (200 ml.) was heated at 60°C. and stirred while potassium permanganate solution (105 ml., 0.27 *M*) was added over a period of one hour. Excess permanganate was decomposed with sodium bisulphite and the manganese dioxide removed by filtration. The filtrate was acidified with sulphuric acid and the resulting precipitate (2.0 gm.) collected. On crystallization from 50% acetic acid it melted at 238°C. Found: C, 52.0; H, 4.09%; neut. equiv., 83.3. Calc. for $C_{11}H_{10}O_7$: C, 52.0; H, 3.96%; neut. equiv., 84.7.

4-Methoxybenzene-1,2,3,4-tetracarboxylic Acid (IX)

The previous methyl tricarboxylic acid (VIII) (1.0 gm.) was dissolved in 5% aqueous potassium hydroxide solution (80 ml.). The solution was heated on a

steam bath and stirred while potassium permanganate solution (242 ml., 0.117 *M*) was added over a four hour period. The excess permanganate was decomposed with bisulphite and the manganese dioxide filtered off. The filtrate was evaporated to a small volume, refiltered, and acidified with concentrated sulphuric acid. The solution was extracted with three successive 50-ml. portions of ethyl acetate. The extract was evaporated to dryness and the residue recrystallized from 50% acetic acid. The tetracarboxylic acid (0.3 gm.) melted at 167–168° with effervescence. Found: C, 45.8; H, 3.00%; neut. equiv., 69. Calc. for $C_{11}H_8O_9$: C, 46.5; H, 2.83%; neut. equiv., 71.

There was no depression of melting point when the above acid was mixed with an authentic sample of 4-methoxybenzene-1,2,3,4-tetracarboxylic acid synthesized from mesitylene as described below.

Isodurene Sulphonic Acid (XVII)

Isodurene (XVI) was prepared by the Grignard methylation of bromomesitylene (XV) according to the directions of Smith (7). The isodurene was then sulphonated as described by Smith and Cass (8).

4-Hydroxybenzene-1,2,3,5-tetracarboxylic Acid (XIX)

The directions given below are a modification of methods outlined in French (4) and German (5) patents for the oxidation and fusion of pseudocumene-5-sulphonic acid.

Isodurene sulphonic acid (15 gm.) and potassium hydroxide solution (5.5 gm. in 250 ml. of water) were placed in a 1 liter three-necked flask equipped with a reflux condenser and stirrer. The flask was heated to 90°C. by a mantle and during vigorous stirring, powdered potassium permanganate (62.8 gm.) was added at such a rate that the temperature did not exceed 95°C. After the addition was complete the oxidation was continued at the stated temperature for a further 24 hr. Excess permanganate was decolorized with alcohol. The manganese dioxide was filtered and washed with two 150-ml. portions of boiling water. The resulting yellow solution was evaporated to dryness and the residue (15 gm.) pulverized. The bulk of the potassium salt was not purified further, but used in the next stage. A small portion of the potassium salt was acidified and extracted with ethyl acetate; the solvent was evaporated and the residue dissolved in a small quantity of hot water. On cooling, the sulphonic acid (XVIII) m.p. 238°C. was obtained, but it was not examined further.

The crude potassium salt of the sulphonic acid (14 gm.) was mixed with potassium hydroxide (40 gm.) and water (5 ml.) and fused at 200–220°C. for five hours in a nickel crucible. The melt was then cooled to a slush, mixed with water (60 ml.), and acidified with concentrated hydrochloric acid. Water (150 ml.) was added and the mixture heated to boiling and filtered. The filtrate was evaporated to dryness and the residue recrystallized from 5% hydrochloric acid (60 ml.). The hydroxy tetracarboxylic acid (6 gm.) melted at 281–282°C. Found: C, 44.4; H, 2.35%. Calc. for $C_{10}H_6O_9$: C, 44.0; H, 2.26%.

4-Methoxybenzene-1,2,3,5-tetracarboxylic Acid

The phenolic carboxylic acid (XIX) (4.0 gm.) was dissolved in sodium

hydroxide solution (25 ml., 10%) under an inert atmosphere (propane). Methyl sulphate (5 ml.) was added at such a rate that the temperature did not rise above 40°C. Three additional portions (5 ml.) of methyl sulphate were added under the same conditions, along with solid sodium hydroxide to always maintain an alkaline solution. The solution was allowed to stand overnight and finally boiled to destroy excess methyl sulphate and to saponify any ester. Precipitated sodium sulphate was filtered off and the acidified solution was extracted with three portions (15 ml.) of ethyl acetate. Purification of the crude acid obtained by evaporation of the solvent was difficult. It was dissolved in sodium bicarbonate solution, filtered to remove insoluble material, and decolorized with charcoal. The solution was acidified with hydrochloric acid and extracted with ethyl acetate as before. Repetition of this process gave a product (1.3 gm.) which melted at 164–166°C. and was identical with the product (IX) obtained previously by oxidative degradation. Found: C, 46.1; H, 2.98%. Calc. for $C_{11}H_8O_9$: C, 46.5; H, 2.83%.

The tetraphenacyl ester of this acid was made in the usual manner by treatment of its sodium salt with phenacyl bromide. On crystallization from alcohol it melted at 189–190°C. with previous softening and darkening. Found: C, 68.0; H, 4.27%. Calc. for $C_{43}H_{32}O_{13}$: C, 68.2; H, 4.25%.

6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid (X)

The procedure followed was the cold oxidation method of Charlesworth, Anderson, and Thompson (1). If the oxidation is carried out at higher temperature, around 60°C., this phthalic acid could not be isolated.

The dioxanylphthalide (III) (6.0 gm.) was dissolved in warm potassium hydroxide solution (300 ml., 3.5%). The solution was filtered and cooled in an ice-water bath. The temperature was maintained at 5–10°C. while a solution of potassium permanganate (24 gm.) in water (700 ml.) was added over a period of one hour. The resulting solution was allowed to regain room temperature and to stand overnight. The manganese dioxide was filtered off, washed with water, and the combined filtrates made just acid with hydrochloric acid with litmus as indicator. The solution was evaporated at a temperature of 65°C. to a volume of about 100 ml. After the solution was cooled, the separated solid, a mixture of organic and inorganic material, was filtered off. The acidic organic material was dissolved in 5% aqueous sodium carbonate solution and filtered. On acidification a dark brown powder (1.5 gm.) precipitated, which was crystallized from dilute alcohol. The light yellow crystals melted at 223–224°C. with effervescence. Found: C, 55.3; H, 4.16%. Calc. for $C_{11}H_{10}O_6$: C, 55.4; H, 4.20%.

If at any time a solution of the phthalic acid became sufficiently acid to darken Congo red paper, only a dark brown tar was precipitated. Presumably the dioxane ring has opened under the influence of the strong acid and some sort of polymer has resulted. This tar could be converted to the phthalic acid by being boiled with 10 times its weight of 10% sodium hydroxide solution and then carefully acidified.

The Anhydride (XI) *and Imide* (XII) *of 6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid*

A mixture of the above phthalic acid (X) (2.0 gm.) and acetic anhydride (20 ml.) was heated on the water bath for one hour. The solution was filtered and allowed to stand in the refrigerator for 24 hr., when the anhydride separated as stout needles (1.3 gm.) of light brown color. These were crystallized from dry toluene and melted at 130°C.

An intimately powdered mixture of the anhydride (2.0 gm.) and urea (2.0 gm.) was heated in an oil bath at 160° until the evolution of ammonia ceased. The molten mixture was poured into boiling water (1 liter) in which it quickly dissolved. Upon cooling the phthalimide separated as orange plates (1.2 gm.) which were crystallized from 50% alcohol. The imide melted at 162°C. Found: C, 60.9; H, 4.13%. Calc. for $C_{11}H_9O_4N$: C, 60.3; H, 4.12%.

Degradation of 6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid (X) *to 1-Methyl-4-methoxybenzene-2,3,5-tricarboxylic Acid* (VIII)

The dioxanylphthalic acid (X) (3.0 gm.) was dissolved in glacial acetic acid (80 ml.) and oxidized with chromic oxide at 65–70°C. by the method described above for the oxidation of the dioxanylphthalide (III). At the end of the oxidation water (600 ml.) was added and the solution evaporated *in vacuo* to dryness. Acidic organic material was dissolved by digestion with 5% sodium carbonate solution (50 ml.) and the resulting solution was then filtered off. Careful acidification of the filtrate gave the crude dioxanonephthalic acid (XIII) in the form of a brown tar. It was not possible to purify this further without hydrolysis of the dioxanone ring, so this was accomplished by boiling the tar for one hour with 10% aqueous sodium hydroxide (30 ml.). Acidification gave a small amount of light brown powder which gave a purplish color with ferric chloride solution and was the hydroxy acid (XIV). It was not purified further, but was methylated in alkaline solution in the usual manner. Upon acidification a small amount of light brown powder, m.p. 229°C. was obtained. It was recrystallized from 50% acetic acid and melted at 234°C. A mixed melting point with a sample of the methoxy tricarboxylic acid (VIII) previously described gave no depression.

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AROMATIC HYDROXYLAMINES AS ORGANO-ANALYTICAL REAGENTS[1]

By G. D. Lutwick and D. E. Ryan

ABSTRACT

The investigation of the use, as analytical precipitants, of a number of aromatic phenylhydroxylamines is described. In general they react similarly, increasing in selectivity with an increase in acidity of the oxime group. In acid solutions (1% or more) only vanadium, tin, titanium, and zirconium are precipitated. Their variation in reaction with copper and the nature of their reaction with tin are described. All compounds can act as oxidants or reductants with an oxidation potential of approximately −1.2 volts.

INTRODUCTION

The use of cupferron [$C_6H_5NO(NH_4)NO$] as an analytical precipitant was first proposed by Baudisch (1). It is most useful in acid medium for the quantitative precipitation of iron, titanium, zirconium, vanadium, and tin; elements such as aluminum, chromium, manganese, nickel, cobalt, and the alkaline metals with which they are usually associated do not interfere. A marked disadvantage of cupferron, however, is its instability. In addition, complexes precipitated by this reagent cannot be weighed as such but must be ignited to the oxides.*

Schome (4), by substituting a benzoyl for the nitroso group of cupferron, obtained a compound that was stable, and formed complexes with iron, aluminum, and copper that could be dried at 110°C. Ryan and Lutwick (3) extended the use of N-benzoylphenylhydroxylamine to the gravimetric determination of tin. The tin complex was dried at 110°C. and weighed as $[(C_{13}H_{10}NO_2)_2SnCl_2]$.

The low solubility of the N-benzoyl derivative of phenylhydroxylamine in water necessitates close control of excess reagent and its basicity prevents the preparation of an ammonium salt. For these reasons a number of N-substituted phenylhydroxylamine compounds, containing a carbonyl alpha to the oxime, were prepared and their reactivities investigated.

COMPOUNDS INVESTIGATED

The following (mono-) N-derivatives of phenylhydroxylamine were prepared: benzoyl ($C_6H_5\overset{O}{\overset{\|}{C}}-$), O-ethoxybenzoyl ($C_8H_9O\overset{O}{\overset{\|}{C}}-$), α-naphthoyl

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**Duval has shown that the cupferrates of iron (Anal. Chim. Acta, 5: 160. 1951) and copper (Anal. Chim. Acta, 6: 47. 1952) are the most stable of the cupferron complexes and that they may be brought to constant weight. Their usefulness as weighing forms, however, is questionable as the iron complex decomposes very rapidly above 98°C. whilst the copper compound is not stable above 107°C.; it is still advisable to ignite these complexes to the oxide.*

$(C_{10}H_7\overset{\overset{O}{\|}}{C}-)$, 3,5-dinitrobenzoyl $(C_6H_3(NO_2)_2\overset{\overset{O}{\|}}{C}-)$, 2,4-dichlorobenzoyl $(C_6H_3Cl_2\overset{\overset{O}{\|}}{C}-)$, O-iodobenzoyl $(C_6H_4I\overset{\overset{O}{\|}}{C}-)$, α-furoyl $(C_4H_3O\overset{\overset{O}{\|}}{C}-)$, benzenesulphonyl $(C_6H_5S(=O)(=O)-)$, and the benzoyl derivative of naphthylhydroxylamine $(C_6H_5\overset{\overset{O}{\|}}{C}-N(\overset{|}{O}H)-C_{10}H_7)$. These compounds were prepared by the addition of their acid chlorides to phenylhydroxylamine in an ether solution containing pyridine (2); 0.05 moles of the hydroxylamine was present in excess of the theoretical in order to decrease the yield of the di-compound $[(R-\overset{\overset{O}{\|}}{C}-)_2ONC_6H_5]$. The compounds were purified by recrystallization from a water–ethanol solution.

Physical Properties

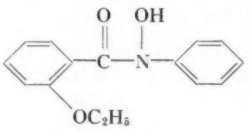
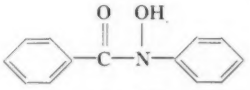
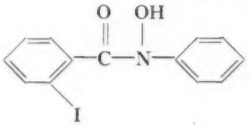
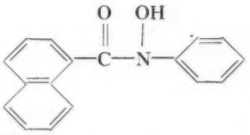
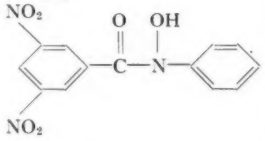
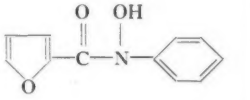
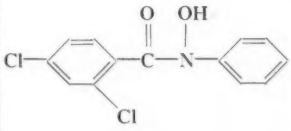
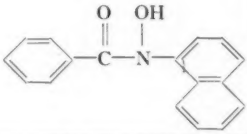
Table I shows the physical properties and structural formula of these compounds. They are soluble in most organic solvents but only slightly in water, the benzoyl derivative showing the highest solubility. The melting points are higher than that of N-benzoylphenylhydroxylamine with the exception of the O-ethoxybenzoyl-derivative; the melting of these compounds is accompanied by decomposition, the material becoming red then black. They can be stored without a preservant for two years or more without any decomposition; this stability is a marked advantage over cupferron.

Chemical Properties

Similar reactions were shown by the compounds of Table I; the benzenesulphonyl derivative did not react. The reactions were carried out by adding 1 ml. of a 1% alcohol solution of the compound under investigation to 100 mgm. of the metal ion in 10 ml. of an acidic and a neutral solution. No color or precipitate was noted with the following: Cr^{+++}, Co^{++}, Zn^{++}, Cd^{++}, Ni^{++}, Mg^{++}, Bi^{+++}, Ag^{+}, Hg_2^{++}, and MoO_4''. In neutral solutions Mn^{++}, Pb^{++}, and Al^{+++} formed white precipitates, UO_2^{++} yielded a yellow precipitate, Cu^{++} a greenish-yellow precipitate, and Fe^{+++} an orange precipitate. In solutions greater than 1 per cent in concentrated hydrochloric acid only Sn^{++++}, Sn^{++}, Ti^{+++}, Zr^{++++} (Hf^{++++}), V^{+++++} (as VO_4''') reacted to give precipitates. The tin and zirconium complexes are white, the titanium yellow, and the vanadium purple in color.

Oxidation–reduction reactions were observed with Cr_2O_7'', MnO_4', V^{++}, and Ti^{+++}. In acid solutions the orange dichromate was reduced to the green chromic ion and the pink color of permanganate was discharged. The violet hypovanadous ion was oxidized in at least two stages passing through the

TABLE I
PHYSICAL PROPERTIES OF THE COMPOUNDS

Compound	Structural formula	Color	M.p., °C.	Solubility in H_2O, gm./ 100 ml.
N-O-Ethoxybenzoylphenyl-hydroxylamine		White	103	0.011
N-Benzoylphenyl-hydroxylamine		White	121	0.040
N-O-Iodobenzoylphenyl-hydroxylamine		White	128	0.010
N-Naphthoylphenyl-hydroxylamine		White	129	0.003
N-3,5-Dinitrobenzoylphenyl-hydroxylamine		Yellow	133	0.007
N-Furoylphenyl-hydroxylamine		White	134	0.013
N-2,4-Dichlorobenzoylphenyl-hydroxylamine		White	137	0.006
N-Benzoylnaphthyl-hydroxylamine		White	164	0.013

green vanadous to the blue vanadyl; from a purple titanous solution the yellow titanic precipitate was formed.

The N-benzoylphenylhydroxylamine compound is too basic to permit the preparation of an ammonium salt. The enhanced acidity of the furoyl-compound enables such a salt to be prepared and aqueous reagent solutions are thus possible.

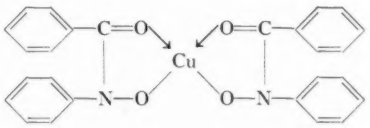
Change of precipitant necessitated a change in acidity for complete precipitation of the common elements. Variations in the acid concentration did not markedly affect the precipitation of the zirconium and vanadium complexes by the different reagents. Vanadium (V) was completely precipitated in 10% concentrated hydrochloric acid solution and zirconium (IV) in 5% by all compounds.

The vanadium complex precipitated by benzoylphenylhydroxylamine decomposed when heated at 110°. Zirconium formed a complex with the empirical formula $[Zr(C_{13}H_{10}NO_2)_4]$ that can be dried at 110°. Titanium was completely precipitated by N-benzoylphenylhydroxylamine in a solution 5% in concentrated hydrochloric acid (4); with the other compounds complete precipitation occurred in solutions only as high as 2% in hydrochloric acid. The complex of titanium was of a variable composition and it is thus not possible to dry to constant weight.

In order to investigate more closely the effects of these substituents, a detailed investigation of the reaction with copper and tin was carried out. These two reactions were investigated as two different types of complexes are involved.

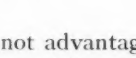
THE COPPER REACTION

Copper reacts with all these compounds by the displacement of the hydrogen of the oxime (shown by a decrease in the pH of the copper solution on adding reagent) to form a planar complex in which the copper is co-ordinatively bonded to the oxygen of the carbonyl.



By measuring the lower pH limit for the complete precipitation of the copper the effect of substituents on the ability to form inner complexes was determined. The results are shown in Table II.

The results show that there is an increase in the pH required for complete precipitation of the copper with an increase in reagent acidity; the furoyl derivative, in which the nature of the ring is changed, is an exception. Therefore attempting to prepare more acidic reagents with this reactive grouping

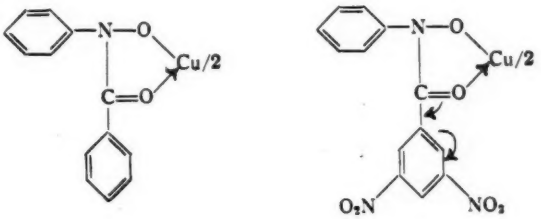


($-C(=O)-N(OH)-C_6H_5$) is not advantageous because the electrons in the carbonyl become so much less available for bonding that precipitates would either not

TABLE II

Compounds	pH of 1% solution of reagent in ethanol	Lowest pH for complete precipitation of copper
N-Benzoylphenylhydroxylamine	7.5	3.0
O-Ethoxybenzoylphenylhydroxylamine	7.3	3.3
O-Iodobenzoylphenylhydroxylamine	7.3	3.0
Naphthoylphenylhydroxylamine	7.2	3.4
2,4-Dichlorobenzoylphenylhydroxylamine	6.8	3.7
Furoylphenylhydroxylamine	6.1	3.0
3,5-Dinitrobenzoylphenylhydroxylamine	5.8	4.2
Benzoylnaphthylhydroxylamine	4.5	5.5

form at all or would only be stable in a basic medium. For example consider the two compounds N-benzoylphenylhydroxylamine and N-3,5-dinitrobenzoylphenylhydroxylamine.



In the nitro-compound there is a shift in the electron density towards these groups so that although the compound becomes more acidic, the electrons on the oxygen of the carbonyl are less available for co-ordination.

THE TIN REACTION

Cupferrón reacts with tin by displacement of the hydrogen of the oxime to form SnC_2 and SnC_4 (C is $C_6H_5\overset{\overset{O}{|}}{N} = O$) type compounds. It was found on analysis that the N-benzoylphenylhydroxylamine reacted with stannous and stannic tin to form compounds containing chloride and were of the same percentage composition (3); for every gram atom of tin there are two gram atoms of chlorine and two gram molecules of the reagent. The melting points of the dried stannous and stannic complexes were identical, 171°C., and mixed melting points gave no deviation. It is apparent that both stannous and stannic tin form the same complex; for this to be true an oxidation–reduction reaction must take place with one of the two ions.

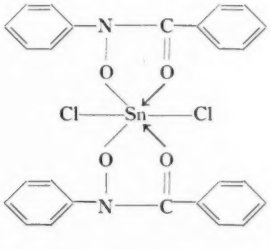
The question of whether an oxidation or reduction has taken place with these reagents has caused some difficulty. Analysis is not sufficient to distinguish between the stannous and stannic complexes which differ only by two hydrogen atoms. Neither pH measurements for determining displacement of hydrogen as the reaction proceeds, nor tests for the oxime grouping in the precipitated compound are suitable to prove or disprove the presence of the oxime hydro-

gen; the tin reaction must be carried out in a fairly acid solution to prevent the formation of metastannic acid and positive tests for the oxime grouping with iron (III) were obtained for the copper complex. Original tests with the –O– methyl ether ($C_6H_5C(=O)-N(OCH_3)-C_6H_5$) derivative indicated that displacement of hydrogen did not take place, but extended investigation has shown that precipitation does not occur with stannic or stannous tin. Attempts to prove reduction by testing for stannous tin and examination of filtrate for oxidized products of the reagents were unsuccessful. Consideration of the oxidizing and reducing properties of these reagents and the corresponding oxidation potentials shown in Table III suggests that tin is reacting in the stannic state.

TABLE III

System	Standard potentials
$V^{+2} \rightarrow V^{+3} + e^-$	0.20
$Ti^{+3} + H_2O \rightarrow TiO^{+2} + 2H^+ + e^-$	−0.1
$Sn^{+2} \rightarrow Sn^{+4} + 2e^-$	−0.15
$H_2O + V^{+3} \rightarrow VO^{+2} + 2H^+ + e^-$	−0.31
$VO^{+2} + 3H_2O \rightarrow VO_4^{-3} + 6H^+ + e^-$	−1.00
$C_6H_5NH_3^+ + H_2O \rightarrow C_6H_5NH_2OH^+ + 2H^+ + 2e^-$	−1.20
$Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^-$	−1.36
$Mn^{+2} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$	−1.52

In Table III the strong oxidizing agents have high negative potentials, and the couple with the more positive potential will be oxidized more readily. On the basis of the oxidation–reduction reactions that these compounds enter into, their oxidation potentials are quite similar to the phenylhydroxylamine–aniline couple (−1.20 volts). The co-ordination number of stannic tin combined with the oxidation potentials of the reagents favor the formation of the following complex.



The N-benzoyl derivative gave complete precipitation in solutions as high as 8% in concentrated hydrochloric acid. The naphthoyl-,2,4-dichlorbenzoyl-phenylhydroxylamine and the benzoylnaphthylhydroxylamine gave complete precipitation in solutions 1% in concentrated hydrochloric acid, whereas the

remainder, O-ethoxybenzoyl, O-iodobenzoyl-, furoyl, and the 3,5-dinitrobenzoyl derivatives gave incomplete precipitation in such solutions. The effect on the tin reaction is more marked than that with copper; this is evident from a comparison of the tin and copper reactions with N-benzoylphenylhydroxylamine and O-ethoxybenzoylphenylhydroxylamine.

CONCLUSIONS

In the preparation of a more acidic reagent in which co-ordination occurs as well as substitution, it is insufficient to consider only the effect of the substituent on the acid grouping of the reagent; it is also necessary to consider the effect on the donor ability of the group which forms the co-ordinate bond. The use of substituents on the ring of the benzoyl group of N-benzoylphenylhydroxylamine failed to improve on this reagent as a precipitant, rather it destroyed the favorable property of being able to precipitate tin from a fairly acid medium.

The formation of the ammonium salt of N-furoylphenylhydroxylamine may prove advantageous for the determination of copper, iron, aluminum, titanium, vanadium, and zirconium as it is readily soluble in water.

An investigation into the effect of substituents on the ring of the phenylhydroxylamine group may be profitable. Substituents on this ring should have more effect on the acidity and less effect on the donor ability because of the increase in distance from the carbonyl although a comparison of the reactions of N-naphthoylphenylhydroxylamine and N-benzoylnaphthylhydroxylamine with copper is not in agreement with this hypothesis. Such a compound might also form a stable ammonium salt.

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ESTIMATION OF IMPURITIES IN LIQUID CHLORINE BY INFRARED ABSORPTION SPECTROPHOTOMETRY[1]

By A. W. Pross

ABSTRACT

Commercial chlorine may contain small amounts of chlorinated organic impurities, some of which have been estimated by infrared absorption spectrophotometry. Liquid chlorine has no infrared absorption spectrum up to 1180 cm^{-1}. This has enabled long path lengths to be used to increase the sensitivity to low concentrations of organic compounds. A 5 cm. tantalum-clad steel pressure cell fitted with calcium fluoride windows was used, and spectra were recorded on a single beam instrument fitted with a calcium fluoride prism. Using extinction coefficients, estimations were made to a few parts per million on impurities such as chloroform, methylene chloride, phosgene, and hexachlorobenzene. The method was checked by known additions to pure liquid chlorine. The estimation of moisture in liquid chlorine is discussed.

Commercial chlorine from the electrolysis of brine in either diaphragm or mercury cells contains small amounts of chlorinated organic impurities. Although such contaminants are present in only a few parts per million, a knowledge of their concentration is of importance to the manufacturer. The impurities appear to be predominantly C_1 and C_2 hydrocarbons such as carbon tetrachloride, chloroform, methylene chloride, and hexachloroethane with, in certain cases, more complex compounds such as hexachlorobenzene. The estimation of these impurities has been difficult, since the analytical methods available were time consuming and required several liters of sample. The most reliable method has been the distillation of approximately 10 liters of liquid chlorine through a fractionating column as described by Hedgepath and Riggs (3) and modified by Matthews and Warren (4). However, distillation methods are at a disadvantage because the chemical nature of the impurity may change during distillation; chloroform for example may chlorinate further to carbon tetrachloride. This disadvantage is absent in a spectrometric method.

Chlorine consists of the molecules Cl_2^{35-35}, Cl_2^{37-37}, and the heterotope Cl_2^{35-37}. The former, in common with other isotopically homogeneous molecules, are transparent to infrared radiation. The molecular heterotope, however, would be expected to absorb, and since its concentration is normally 36.6% this absorption cannot be ignored (2). The fundamental band has been calculated to be at 554 $cm.^{-1}$ in the gas phase, with first and second overtones at 1100 $cm.^{-1}$ and 1638 $cm.^{-1}$ respectively. In liquid chlorine the absorption frequencies of these bands would be lowered by about one half of one per cent (1). The fundamental and the first overtone are beyond the range of calcium fluoride transmission. No band at around 1640 $cm.^{-1}$ corresponding to the second overtone has been detected.

[1]*Manuscript received June 17, 1954.*
Contribution from Canadian Industries Limited, Central Research Laboratory, McMasterville, Que.

EXPERIMENTAL

Wright and Smith employed a 1-in. tantalum-clad brass pressure cell with quartz windows for the estimation of moisture at 3700 cm.$^{-1}$ (7). This cell was limited by the cutoff of quartz at 2850 cm^{-1}. For the following work a 5.25 cm. tantalum-clad steel cell was used with calcium fluoride windows which are transparent in the infrared as far as 1180 cm^{-1}. The extreme transparency of liquid chlorine in the infrared has enabled the use of a path length which is approximately two thousand times greater than is usual for most organic liquids. This path length has caused the method to be sensitive to concentrations of absorbing substances of the order of a few parts per million. This cell was designed and made by the Perkin–Elmer Corporation (5).

A section of the cell is shown in Fig. 1. It consists of a $1\frac{3}{4}$ in. diameter steel cylinder 2 in. long, clad with tantalum which is resistant to liquid chlorine

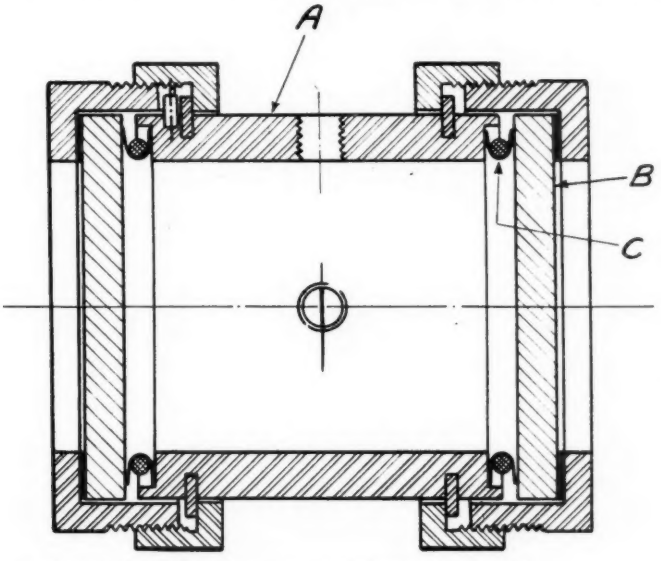

FIG. 1. Section of the Perkin–Elmer 5 cm. tantalum-clad steel cell.
A. Tantalum-clad steel cylinder.
B. Calcium fluoride window.
C. Rubber gasket in "Teflon" envelope.

(*A*). The windows are $\frac{1}{4}$ in. thick calcium fluoride (*B*). "Teflon" U-Section gaskets are used with neoprene O-ring inserts (*C*). The windows are secured by means of caps which are drawn against them. They are protected by $\frac{1}{8}$ in. diameter keys which prevent the caps from turning. The cell is designed for a pressure of 200 p.s.i. The vapor pressure of chlorine at 25°C. is 105 p.s.i. gauge.

The cell was fitted to a stainless steel reservoir and a valve system consisting of $\frac{1}{8}$ in. stainless steel "Hoke" needle valves. This makes possible the filling

of the cell with liquid chlorine directly from an inverted commercial cylinder without cooling. Alternatively, by placing the reservoir in a Dewar flask packed with dry ice, liquid chlorine could be introduced from a flask as shown in the line diagram Fig. 2. As a precautionary measure the nitrogen inlet tube at *A* was held in place by hand so that it could be instantly released should excessive back pressure develop because some part of the system was insuffic-

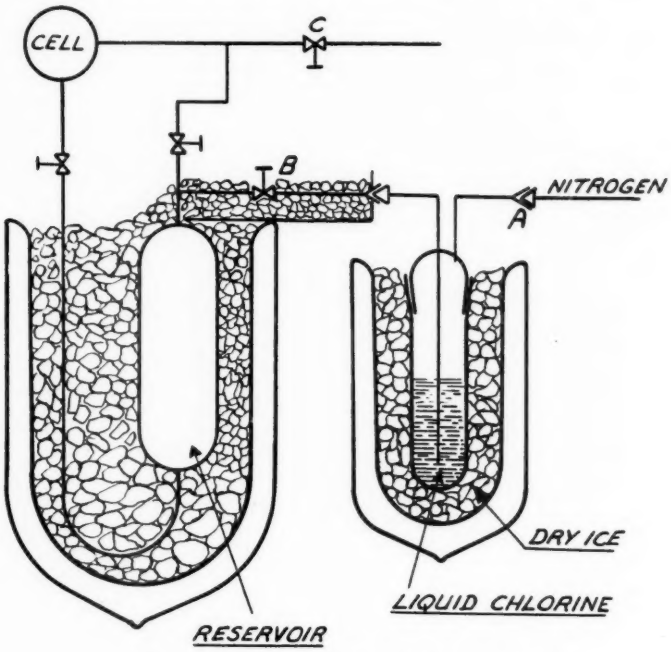

FIG. 2. Diagram to show method of filling reservoir.

iently cooled. After the reservoir had been filled, the dry ice packing around the inlet tube was removed. Valves *B* and *C* were then closed, and the reservoir was removed from the Dewar. Before the reservoir was inverted, the system was brought to room temperature with the help of lukewarm water. This avoided possible fracture of the windows which might have resulted if cold chlorine were allowed to enter the cell. When filled, the reservoir and cell were supported in front of the entrance slit of the spectrometer.

Spectra were recorded on a Perkin–Elmer Model 12C single beam instrument using a calcium fluoride prism. The increased resolution afforded by a calcium fluoride over a rock-salt prism is an advantage in this work.

The specific extinction coefficient E_ν is given by the Lambert-Beer relationship:

$$E_\nu = \frac{1}{cl} \log\left(\frac{I_0}{I}\right)_\nu \text{max} \qquad [1]$$

where c = concentration in gm. per ml.,
l = path length in cm.,
I_0 = intensity of incident radiation,
I = intensity of absorbed radiation.

In this work band intensities are a function of the experimental conditions. Apparent specific coefficients E_ν^a have therefore been quoted, following the example set by Ramsay (6). The incident and absorbed radiation intensities were taken as proportional to the background and band peaks respectively. Finite slit width and scatter corrections were dispensed with. Band intensities thus measured gave estimations of impurities which were accurate to between 10% and 20%.

Formula (1) was rearranged and parameters were substituted to give concentrations in parts per million from a constant multiplied by the optical density. The method was tested by addition of known quantities to liquid chlorine. The liquid chlorine used in these experiments was purified by distillation using a column packed with "Fenske" rings having a performance equivalent to approximately eight theoretical plates and a reflux to product ratio of 2: 1. A spectrum was first recorded to ensure the absence of impurities, after which the chlorine was distilled back into the flask surrounded by dry-ice. Volatile compounds such as chloroform and methylene chloride were added from a weighing pipette, and solids were added as such with subsequent agitation until dissolved. Recording time for the spectrum over the range 4000 cm.$^{-1}$ to 1180 cm.$^{-1}$ was approximately 30 min.

Table I summarizes the analytical results obtained with this technique. The frequencies of the analytical bands are those observed for the compounds

TABLE I
SUMMARY OF ANALYTICAL RESULTS

Compound	ν, cm.$^{-1}$	E_ν^a	Concentration in p.p.m.	
			Added	Found
$CHCl_3$	1216	900± 75	61	56
			106	100
CH_2Cl_2	1259	1320± 30	57	46
C_6Cl_6	1348	4900±600	10	11
			20	18

in liquid chlorine as solvent. Further analytical bands of interest, with their frequencies and apparent extinction coefficients, are given in Table II. For concentrations that may be encountered in practice no suitable bands are

TABLE II
ANALYTICAL ABSORPTION BANDS AND APPARENT EXTINCTION COEFFICIENTS

Compound	ν, cm.$^{-1}$	E_ν^a
$CH_2ClCOCl$	1821	4400±100
$COCl_2$	1810	6080±110
H_2O	1640	1010± 20

present in the range 400 cm.$^{-1}$ to 1180 cm.$^{-1}$ for carbon tetrachloride or hexachloroethane. Analysis for these compounds will depend on finding a suitable cell window material that will transmit further into the infrared.

WATER

Analytical estimations by this method are under investigation. The absorption band at 1640 cm.$^{-1}$ has an advantage over the 3700 cm.$^{-1}$ band used by Wright and Smith as there is no correction required for carbon dioxide. Any interference in the 1640 cm.$^{-1}$ region would be from amide–carbonyl and C=C unsaturation; and neither would be expected in liquid chlorine. The vaporizing of sufficient liquid chlorine into a gas cell as a means of correction for carbon dioxide is open to criticism as carbon dioxide boils off first resulting in a false value for this correction.

ACKNOWLEDGMENTS

The constant help and advice of F. W. Matthews of this laboratory is gratefully acknowledged, as is also the distillation work carried out by G. G. Warren, also of this laboratory. The Perkin–Elmer Corporation is thanked for the loan of the cell.

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THE QUENCHING OF POTASSIUM RESONANCE RADIATION BY HYDROGEN AND DEUTERIUM[1]

By W. M. Smith, J. A. Stewart,[2] and G. W. Taylor[3]

ABSTRACT

The quenching of the resonance radiation of potassium by hydrogen and deuterium has been studied over the temperature range 71°C. to 83°C. The quenching cross sections at 76°C. were found to be 1.56×10^{-16} cm.^{2} and 1.10×10^{-16} cm.^{2} respectively.

INTRODUCTION

Among the simplest processes involving quenching of excited atoms are those involving the various alkali metals in their lowest ^{2}P state and molecular hydrogen as quencher. Experimental studies have been restricted in the past to sodium. We have attempted to obtain cross sections for the quenching of excited potassium, $4^2P\rightarrow4^2S$, by hydrogen and by deuterium with a view to obtaining further data relating to systems relatively amenable to theoretical examination.

METHOD

The experimental method resembled that used by Steacie and LeRoy (8). Two resonance vessels containing potassium were housed together in a furnace and irradiated by a beam with a substantial portion of the radiation consisting of the doublet λ7665 Å and λ7699 Å. Quenching gas was added to one vessel; the other vessel served as a reference. The relative intensities of the resonance radiation emitted from the two vessels at right angles to the irradiating beam were estimated with a photoelectric photometer. Measurements made in the absence and in the presence of quenching gas yielded the quenching ratio, Q, which is defined as the ratio of the intensity of resonance radiation in the presence of quenching gas to the intensity of resonance radiation in the absence of quenching. The quenching cross section, σ^2, in cm.^{2} may be calculated from the slope, S_Q, of the plot of $1/Q$ against p (in mm. Hg) using the relation (5),

$$\sigma^2 = S_Q/2666.4\tau\left[\frac{2\pi N}{kT}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right]^{\frac{1}{2}}$$

where τ is the mean life of the potassium atom in the 4^2P state which we have taken to be 2.71×10^{-8} seconds (9), N is Avogadro's number, k is the gas constant in ergs per molecule per degree, and M_1 and M_2 are the gram molecular weights.

[1]*Manuscript received June 21, 1954.*
Contribution from Department of Chemistry, Queen's University, Kingston, Ontario.
[2]*Milton Hersey Fellow, Queen's University, 1951–52. Present address: Department of National Health and Welfare, Food and Drugs Division, Ottawa.*
[3]*Holder of an Ontario Research Council Scholarship, 1952–53. Present address: The University Chemical Laboratory, Cambridge, England.*

The two resonance vessels were constructed of tubing $2\frac{1}{2}$ cm. in diameter and were about 13 cm. long. They were of the usual light trap type with two plane windows meeting at right angles to facilitate entry of the irradiating beam and exit of a portion of the fluorescent radiation at right angles to the beam. The vessels were centrally mounted one above the other in a furnace about 28 cm. long containing double windows placed appropriately for entry and exit of the radiation referred to above. The interior of the furnace was blackened as were also the masks within the furnace which were used to demarcate the irradiating and fluorescent radiation. The resonance vessels used during the initial measurements were of quartz, during the final measurements of pyrex. The quenching vessel was connected via a stopcock outside the furnace to a wide bore mercury manometer, storage bulbs, MacLeod gauge, and pumping system. A cathetometer was used to read the levels of the manometer. A magnetic cutoff operating within the furnace in the line connecting the quenching vessel to the rest of the vacuum system was incorporated in the apparatus during the early measurements but was omitted in the later measurements. The reference vessel was permanently sealed. The portion of the vessel containing the windows was free of potassium deposit but that portion immediately adjacent was covered with a deposit around the entire inner circumference. Inspection of the vessels, with local heating if necessary, was carried out every few days to ensure that this distribution of potassium was maintained. Temperature differences of the order of 1°C. existed within the furnace. However the difference in temperature between the region containing the resonating vapor under observation and the site of potassium probably did not exceed 1/3°. The region of the vessel containing the windows and the resonating vapor under observation was at the highest temperature. The temperature was held constant during a run to within 0.1°C.

The source of the irradiating beam was a K-1 General Electric potassium lamp. The radiation from the lamp passed through a rectangular slit in a blackened mask, through a Corning filter number 2600 and a system of lenses which formed an image of the slit in the front portion of the resonance vessels. The beam was further restricted by a blackened mask containing two rectangular holes which was placed immediately in front of the resonance vessels. To check approximately the changes in intensity of the irradiating beam and so permit estimates to be made of the variation in intensity of the reflected radiation associated with the fluorescent beam, a Weston photronic cell was mounted so that it could be swung into the path of the irradiating beam. Although the sensitivity of the photronic cell to the radiation in the beam is very low, sizable deflections were obtained with a galvanometer in series with the photronic cell. Measurements of this sort were required only because of the relatively appreciable magnitude of the reflected radiation accompanying the fluorescent radiation and were used only when estimating the magnitude of the reflected radiation.

The fluorescent radiation emerging from openings in a mask covering the exit windows of the resonance vessels was focused on the sensitive surface of a RCA 917 phototube. As the eye is relatively insensitive to wave lengths around

7700 Å, a small flash light bulb was mounted under the resonance vessels, and was turned on during initial focusing operations. The phototube and the associated circuit, which was that devised by Gabus and Pool (2), was enclosed in a brass tube fitted with a shutter which permitted the focused fluorescent radiation from either resonance vessel to fall separately on the phototube. The amplified photocurrent was determined with a Rubicon galvanometer No. 3403. In subsequent paragraphs the setup involving phototube, amplifier, and galvanometer is called the detector. The correlation between light intensity and response of the detector was determined at intervals throughout the runs with calibrated neutral filters and invariably the detector showed response linear with light intensity. As a dark room was not available the entire optical system was housed in blackened boxes and all measurements were carried out at night.

The resonance radiation from the resonance vessels was examined spectrographically and only the 7699–7665 doublet appeared on the photographic plate.

MATERIALS

Hydrogen and deuterium were prepared by the action of light or heavy water on potassium. Distilled water, deaerated by several cycles of freezing, melting, and pumping off *in vacuo*, was distilled into an evacuated bulb of about 300 cc. capacity containing purified potassium and fitted with a mercury manometer of the blowoff type. The gas from the reaction bulb was passed slowly through two traps refrigerated with liquid air, and was then stored for a minimum of 24 hr. in a flask containing a film of potassium on the walls.

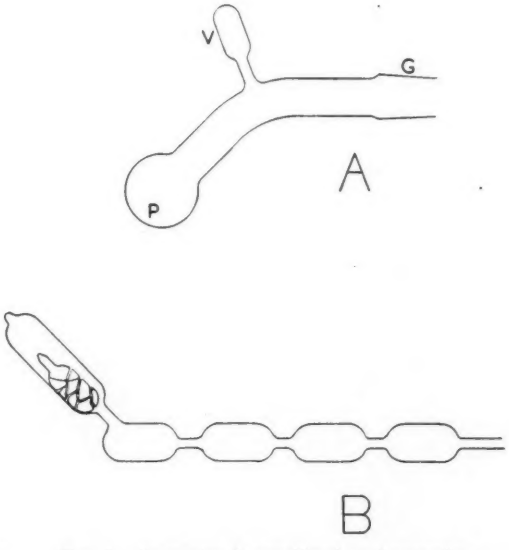

FIG. 1. Apparatus for purification of potassium.

The 99.6% heavy water was obtained from Atomic Energy of Canada Ltd.

The potassium was purified as follows. The surface film was cut off B.D.H. lump potassium, the metal was blotted dry with filter paper and then introduced into the unit indicated in Fig. 1A. This consisted essentially of a wide diameter tube bent to an angle of about 135° and connected horizontally to the vacuum system and traps via the ground joint *G*. One or two small vials *V* were connected to the larger tube at the bend and roughly in the same plane as the large bent tube. With potassium resting in the bottom of the tube at *P* the unit was connected to the vacuum system and evacuated. The potassium was then heated with refluxing until there was no evidence of gas evolution. The unit was then rotated and liquid potassium flowed into the vials at *V*. These were sealed off. Potassium from these vials was introduced into the vacuum apparatus where and when required by the technique of Dunoyer (1). This involved crushing the vial and quickly sealing it in the end bulb of a series of bulbs connected by short yet thick walled tubes, the whole series leading to the final site. These are illustrated in Fig. 1B. The end bulb was placed at a slant to facilitate the separation of potassium from the crushed vial and its entry into the second bulb without distillation. After entry of potassium into the second bulb *in vacuo*, the end bulb was sealed off and potassium was distilled *in vacuo* from one bulb into the next, the end bulb containing some residue of potassium being sealed off before the next distillation in the chain was carried out.

PROCEDURE

After the quenching vessel had been evacuated and the potassium lamp had been operating for more than one hour, measurements of the intensities of the radiation from quenching and reference vessels were made with the detector. Quenching gas was then added in steps and withdrawn in steps. Measurements of the pressure of gas in the quenching vessel and of the intensities of the radiation from each of the resonance vessels were made after each addition or removal of gas. It was found that there were no significant changes in intensity of radiation from the resonance vessel after about three minutes after addition of gas. In practice periods of 5 and 10 min. were allowed to elapse between addition of gas and taking of measurements. The quenching ratios obtained on addition and removal of gas were not significantly different.

At the conclusion of a quenching run the furnace was allowed to cool to room temperature and with the potassium lamp operating under steady conditions detector measurements were made of the intensities of the reflected radiation from the quenching vessel. As the vapor pressure of potassium at 36.4°C. is about 0.03 of the vapor pressure at 71°C. and as the intensity of the radiation from the resonance vessels was not detectably dependent on temperature at temperature less than 35°C. it is legitimate to conclude that the intensity of resonance radiation at room temperature relative to that at 76° (the mean temperature during the experiments) is negligible. These measurements indicated that the reflected radiation constituted from 5 to 20%

of the radiation emitted from the resonance vessel, the higher figure applying to the earlier measurements involving the quartz vessel. Measurements of the intensity of the irradiating beam were also made with the photronic cell inserted directly into the beam so that sizable variations in beam intensity and therefore in reflected radiation between hot and cold runs could be detected and allowed for. In fact the effect of such corrections on the allowance for reflected light was negligible.

Variations in the intensity of the irradiating beam or small variations in the concentration of potassium vapor due to change in furnace temperature would change the detector reading for radiation from reference and quenching vessel proportionally. Consequently the readings of intensity for radiation from the quenching vessel during a single run were corrected by dividing by a factor proportional to the reference vessel reading. The readings obtained in the initial stages of a run were arbitrarily chosen as standard to which the other readings were adjusted. From these adjusted values, the intensity of reflected radiation (determined in the cold run and adjusted on a proportional basis for variation in intensity of irradiating beam between the cold run and the initial measurements of the hot run) was subtracted. From these final values for fluorescent intensity the quenching ratios were obtained by dividing the intensity applying for a given pressure of added gas by the intensity applying for no added gas.

EXPERIMENTAL RESULTS

Considerable difficulty was encountered in obtaining quenching curves which were reproducible and independent of the position in the quenching vessel of the volume of potassium vapor which yielded the radiation which was measured. It was found essential to have the deposit of potassium within the body of the resonance vessel. Moreover, with the quartz vessel, an approach to reproducibility could be obtained only when the fluorescent radiation came from a volume relatively near the source of potassium. When the resonance radiation came from a region close to the front face of the vessel and relatively distant from the source of potassium plots of the measured values of $1/Q$ against pressure, P, yielded curves bending away from the P axis. At temperatures above 90°C. this effect was observed regardless of the positions of the resonating potassium vapor yielding the radiation which was measured. The effect became more pronounced with use of the resonance vessel. Apparently the concentration of potassium vapor was being reduced below its equilibrium value by reactive processes and this reduction was leading to abnormal drops in the intensity of the resonance radiation.

On the other hand the results obtained with the pyrex vessel were reproducible and independent of thickness of the fluorescent beam over the range of temperature 71 to 80°C. No attempts were made to examine the behavior at temperatures in excess of 80°C. or at less than 71°C. The independence of quenching ratio on the vapor pressure of potassium over the 9 degree range and on the thickness of the fluorescent beam suggests that effects due to imprisonment are negligible.

The experimental results are given in Fig. 2 as plots of $1/Q$ against pressure. The results include data from all runs with the pyrex vessel except one which was omitted because of poor distribution of potassium in the vessel. There are included data from a small group of runs in the quartz vessel selected on the basis that they yielded the smallest $1/Q$ values. The thickness of the fluorescent beam under observation ranged from 2 to 5 mm. There appears to be no significant change in slope of $1/Q$ against pressure over the temperature range 71 to 83°C. However there should be a small dependence of $1/Q$ (for a

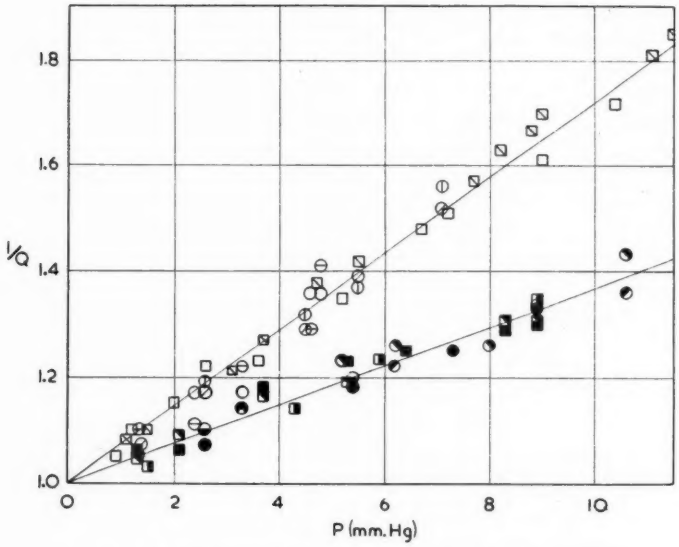

Fig. 2. $1/Q$ for various pressures of hydrogen and deuterium

Data for hydrogen			Data for deuterium		
	Quenching Vessel	Temperature °C.		Quenching Vessel	Temperature °C.
□	quartz	74	■	quartz	71
□	quartz	83	◪	quartz	71
○	pyrex	71	◨	quartz	76
⊖	pyrex	71	●	pyrex	71
⊕	pyrex	76	◒	pyrex	71
⊘	pyrex	76	◔	pyrex	80
			◐	pyrex	80

given pressure) on temperature if the cross section for quenching is independent of temperature because of the variation in concentration and molecular velocity with temperature. It is possible to correct the values of $1/Q$ to a common basis, that for T_{ret}, by multiplying each value of $(1/Q-1)$ by $(T/T_{ret})^{\frac{1}{2}}$ where T is the absolute temperature at which the determination was made. However in view of the smallness of the corrections (less than one per cent) and the relatively low precision of our results we have not applied this correction. From the slope of the $1/Q$ vs. P plot of Fig. 2, 76°C. as the temperature, 2.71×10^{-8} seconds as the value of τ, we have determined that σ^2 for hydrogen is 1.56 Å^2 and σ^2 for deuterium is 1.10 Å^2.

DISCUSSION

The cross section for the quenching of excited sodium atoms by hydrogen is substantially larger than the cross section 1.56 Å^2 which we have found for the quenching of excited potassium. Norrish and Smith (6) found a cross section of 7.4 Å^2 at a temperature of 130°C. with sodium excited by the resonance method similar to that employed in the present work. Winans (10) using high velocity excited sodium atoms produced by the photodissociation of sodium iodide found that the cross section for quenching by hydrogen decreased with increasing velocity of the sodium atoms and attained a value of 5.7 Å^2 for the maximum velocity investigated which was about 10 times the mean velocity at 130°C.

Magee and Ri (4) and Laidler (3) have attempted theoretical calculations of the cross section for quenching of excited sodium by hydrogen. Both treatments describe the process in terms of the formation of a relatively stable complex of alkali metal and hydrogen and a transition to the ground state during the life of the complex with a probability close to unity. In Magee and Ri's treatment the critical state corresponds to the top of the rotational energy barrier for the formation of a complex involving excited alkali metal and hydrogen. In estimating the cross section it is assumed that complexes with rotational energy below a certain value have during their lifetime a probability of transition to the ground state (via an ionic state) near unity, but that the probability is zero if the rotational energy exceeds this value. In Laidler's treatment the cross section for quenching is identified with the square of the separation of centers of Na (^{2}P) and H_2 which, with the minimum potential energy, permits contact of the excited and the ionic (Na^+ H_2^-) potential energy surfaces. A slight extension of the H—H bond which nevertheless involves insignificant activation energy must be assumed and the critical separation for contact of the surfaces is identified with that corresponding to the minimum in the potential energy curve for the ionic state (Na^+ H_2^-) where the H—H separation is constrained to the slightly extended value. This configuration permits formation of an ionic complex and it is assumed that the probability of transition to the ground state is very much greater than the probability of decomposition of the complex so that once the ionic complex is formed the probability of internal quenching is close to unity.

Magee and Ri indicate that the cross section for quenching of excited potassium should be less than that for sodium. Laidler's treatment suggests the converse since the greater diameter of the potassium ion should lead to a slightly greater critical separation for alkali metal and hydrogen. Our results appear to contradict Laidler's treatment. However an energy of activation for the attainance of the critical state or a probability of transition to the ground state during the life of the complex of appreciably less than unity could lead to a reduced cross section for the quenching of excited potassium. It is impossible, by the technique used in this work, to determine experimentally the activation energy for quenching processes involving potassium. However, the work of Smith and Southam (7) indicated no appreciable activation energy for the quenching of excited sodium with methane, a process with very small cross section, and as far as we can determine there appears to be no evidence for any quenching process which does have an activation energy. The probability of internal quenching during the life of the complex depends on the life time of the complex, the availability of those configurations of the ionic complex from which transitions to the ground state can occur and on the probabilities of the transitions. This appears to be a problem for theoretical rather than experimental examination.

Our data indicate a cross section for quenching by deuterium which is less than that for hydrogen. This cannot be attributed to a difference in potential energy relations, nor does it appear that the difference in zero point energies of critical complex and "reactants" would favor the formation of the complex of hydrogen and potassium above that of the more massive deuterium–potassium complex. The difference in cross sections would appear then to be attributable to differences in the probability of transition between states during the life time of the complex.

ACKNOWLEDGMENTS

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KINETICS OF THE HOMOGENEOUS REACTION BETWEEN CUPRIC ACETATE AND MOLECULAR HYDROGEN IN AQUEOUS SOLUTION[1]

By R. G. Dakers[2] and J. Halpern

ABSTRACT

Cupric acetate was found to react homogeneously with molecular hydrogen in aqueous solution according to the following equation:

$$2Cu(OAc)_2+H_2+H_2O\rightarrow Cu_2O+4HOAc.$$

The paper describes a kinetic study of this reaction. Rates were determined at temperatures between 80 and 140°C. and hydrogen partial pressures between 6.8 and 34.0 atm. The reaction was found to be of second order, the rate being proportional to the concentrations of cupric acetate and molecular hydrogen. It was established that the rate was independent of the surface of the reaction vessel, the cuprous oxide product and of the concentrations of sodium acetate and acetic acid in the solution. The reaction has an activation energy of 24200 cal. per mole. The kinetic results are discussed and a mechanism is proposed. This appears to be one of the few known homogeneous reactions of molecular hydrogen in solution.

INTRODUCTION

Molecular hydrogen is a relatively unreactive gas. Its homogeneous reactions are often characterized by large activation barriers which reflect the high dissociation energy of the H—H bond and the repulsion forces associated with the closed shell configuration of the H_2 molecule in its ground state.

Many substances are known which lower the activation energies of hydrogenation reactions and thus function effectively as catalysts for these reactions. With few exceptions such catalysts are solids, common examples being the group of metals which includes Ni, Co, Pt, and Pd and certain metallic oxides such as CuO, Cr_2O_3, ZnO, and their mixtures (3). The action of these catalysts has been widely studied particularly with reference to organic hydrogenation reactions some of which are of great industrial importance. Nevertheless the detailed mechanism by which they operate is still not fully understood. It is generally believed that the primary function of the catalyst is to activate the hydrogen through chemisorption (3, 19). The catalyzed reaction then occurs heterogeneously. In some cases the catalyst may also serve to activate the reactant undergoing hydrogenation. Theories have been advanced which relate the activity of hydrogenation catalysts to their lattice spacing (1, 2) and to the character of their electronic bands (6, 21). These theories generally imply that catalytic activity, associated with the ability to activate molecular hydrogen, is confined to solids.

Recently there has been increasing interest in inorganic hydrogenation reactions involving the reduction of metallic ions in aqueous solutions. Reactions of this type have found important metallurgical application as methods of recovering metals from leach solutions (7, 8). The reduction of ions such as

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Ni^{++}, Co^{++} (14), UO_2^{++} (8), and VO_3^- (16) has been examined kinetically. All these reactions were shown to proceed heterogeneously and to require the presence of hydrogenation catalysts of the usual type such as finely divided metallic nickel or cobalt.

Of special interest is the reduction of cupric acetate in aqueous solution. Ipatieff and Werchowsky (11) first observed this reaction and reported that cuprous oxide was formed as the product under certain conditions. Recent work in this laboratory has confirmed that this reaction takes place at relatively low temperatures and hydrogen partial pressures and that unlike most hydrogenation reactions it does not require an added catalyst but proceeds homogeneously in solution (10). The present paper describes a kinetic study of this reaction, undertaken with a view to establishing its mechanism and determining the nature of the process through which the hydrogen becomes activated.

Only two other systems involving homogeneous hydrogenation reactions in solution appear to have been studied. Calvin (4, 5) found that cuprous acetate, dissolved in quinoline, catalyzed the homogeneous hydrogenation of compounds such as quinone. It has been suggested (5, 24) that in this system the hydrogen becomes activated through homogeneous interaction with a dimeric complex of cuprous acetate. The solvent appears to play an important role in this process since the reaction is confined to a narrow group of nitrogen containing solvents.

Recently Wender and his co-workers (17, 25) have reported that dicobalt octacarbonyl, $Co_2(CO)_8$, which is formed when metallic cobalt is treated with carbon monoxide at high pressures, also activates hydrogen and thus functions as a homogeneous catalyst in a variety of hydrogenation reactions. The activity of this catalyst like that of cuprous acetate has been observed only in certain organic solvents. The reduction of cupric acetate, described in this paper, appears to be the first instance of a homogeneous hydrogenation reaction reported to occur in aqueous solution.

EXPERIMENTAL

Materials

Cupric acetate, sodium acetate, ammonium acetate, and acetic acid, all of Reagent Grade, were supplied by Nichols Chemical Co. The solutions were prepared by dissolving weighed quantities of these chemicals in distilled water. Commercial hydrogen gas, supplied in cylinders by Canadian Liquid Air Co., was used without further purification.

Apparatus

The experiments were conducted in an autoclave manufactured by Autoclave Engineers Inc. and constructed entirely of No. 316 stainless steel which proved inert to the solutions used. The vessel had a capacity of 1 gal. and was designed for working pressures of up to 1200 lb. per square inch. A stirrer shaft, thermocouple well, cooling coil, and sampling tube extending below the surface of the solution, were connected through the lid of the autoclave.The

solution was stirred with an impeller of 2.5 in. diameter which rotated at 900 r.p.m. The sampling tube was fitted with a stainless steel filter of fine porosity so that samples of solution withdrawn for analysis were free of cuprous oxide product. The partial pressure of hydrogen above the solution was controlled by a standard gas regulator. The autoclave was heated with a gas ring burner, the temperature of the solution being maintained to within $\pm 0.5°$ C. with a Leeds and Northrup Micromax recording controller.

Procedure

Three liters of solution of desired composition was placed in the autoclave which was then sealed, flushed with nitrogen, and heated to temperature. Hydrogen was introduced and maintained at a desired partial pressure. Samples of the solution were withdrawn periodically and the concentration of unreacted cupric acetate determined with a Beckman DU Spectrophotometer using the blue cupric ammine color developed by addition of ammonia. The experiments were generally continued until about 98% of the cupric acetate had reacted. The charge was then removed from the autoclave and the cuprous oxide product separated by filtration, washed, and analyzed.

RESULTS

Stoichiometry of the Reaction

The solutions of cupric acetate used in these experiments generally contained about 0.5 M./liter of acetic acid and 0.5 M./liter of either sodium or ammonium acetate, added to buffer the pH of the solutions at a value between 4 and 5. Attempts to study the reaction in the region of higher pH were complicated by hydrolysis of cupric acetate and precipitation of basic cupric salts when the solutions were heated to the reaction temperature.

On introduction of hydrogen into the autoclave, a visible precipitate of cuprous oxide was immediately formed. As the reaction proceeded the cupric acetate concentration and the pH of the solution both decreased progressively, reflecting the formation of cuprous oxide and acetic acid as the reaction products. The reaction proceeded in every instance until the amount of copper remaining in solution was less than 0.003 M./liter, which corresponds to about 1 or 2% of the original cupric acetate concentration. Because of the buffering action of the acetate the pH drop during an experiment was usually less than 0.5 units.

The cuprous oxide product was identified by chemical analysis (Cu: found, $88.5 \pm 0.3\%$; theoretical, 88.8%) and by X-ray diffraction measurements (lattice constant: found, 4.25 ± 0.01Å; given (13), 4.255Å). In no experiment could any reduction products of cupric acetate, other than cuprous oxide, be detected.

An observation of some interest was that the appearance of the cuprous oxide product differed, depending on whether the solution contained sodium acetate or ammonium acetate. If the solution contained sodium acetate, the product was bright red while if it contained ammonium acetate, the color ranged from dark purple to black. Both products were crystalline solids

apparently identical in chemical composition and crystal structure. The difference in color was presumably due to differences in grain size. Reference has recently been made (12) to similar variations in the appearance of cuprous oxide prepared by other methods.

The stoichiometry of the reaction appears to be represented by the following equation:

$$2Cu(OAc)_2 + H_2 + H_2O \rightarrow Cu_2O + 4HOAc. \qquad [1]$$

When hydrogen was present in excess this reaction always went essentially to completion. The solubility of the cuprous oxide product was negligible.

Kinetics of the Reaction

Rate curves depicting the course of some typical experiments, throughout which the temperature and hydrogen partial pressure were held constant, are shown in Fig. 1. The cupric acetate concentration always fell off according to a first order kinetic law, illustrated by the linear plots of log $[Cu(OAc)_2]$ against time in Fig. 2. First order rate constants, k_1, calculated from the slopes of these plots were generally reproducible to within $\pm 5\%$.

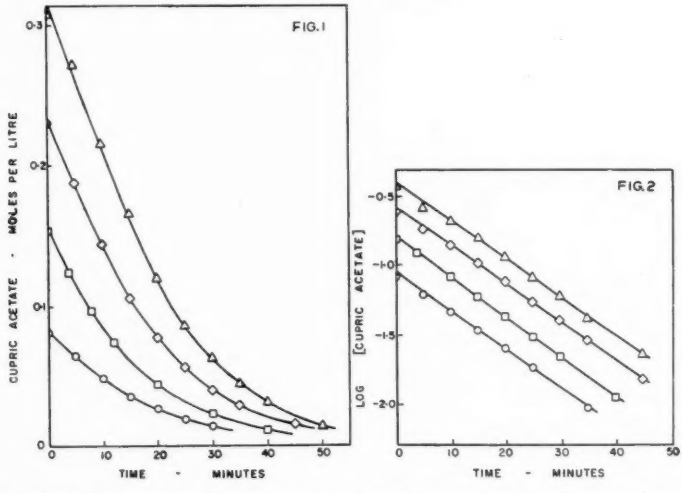


FIG. 1. Typical rate curves for the reaction of cupric acetate with hydrogen. Temperature, 130°C. H_2 partial pressure, 13.6 atm.

FIG. 2. Typical first order rate plots showing effect of varying initial cupric acetate concentration.

Further indication of first order kinetic behavior is provided by data in Table I which show that values of k_1 determined in this way are independent of the initial cupric acetate concentration. The rates were also found to be independent of the volume of solution and of the speed of rotation of the stirrer above 500 r.p.m.

Data are also provided in Table I which show that the rate of reaction remained essentially constant when the pH of the solution and the concentrations

TABLE I

EFFECT OF VARYING THE COMPOSITION OF SOLUTION ON THE RATE OF REACTION BETWEEN CUPRIC ACETATE AND HYDROGEN

Temperature, 130°C.
H_2 partial pressure, 13.6 atm.

$Cu(OAc)_2$, M./liter	NH_4OAc, M./liter	NaOAc, M./liter	HOAc, M./liter	pH		k_1, $min.^{-1}$
				Initial	Final	
0.08	0	0.25	0.31	4.6	4.5	0.0614
0.16	0	0.25	0.38	4.5	4.1	0.0668
0.24	0	0.25	0.44	4.5	4.1	0.0643
0.32	0	0.25	0.40	4.5	4.1	0.0632
0.24	0	0.43	0.64	4.5	4.2	0.0629
0.24	0.25	0	0.10	5.1	4.3	0.0613
0.24	0.50	0	0.18	5.1	4.6	0.0617
0.24	0.75	0	0.26	5.1	4.7	0.0617
0.24	0	0.25	0.29	4.8	4.3	0.0631
0.24	0	0.25	0.44	4.5	4.1	0.0643
0.24	0	0.25	1.17	4.0	3.8	0.0691
0.24	0	0.25	2.35	3.7	3.6	0.0696

of sodium acetate and ammonium acetate were varied over a considerable range. On the basis of these results it can be assumed that the rates were not influenced by the much smaller changes in pH which occurred during the course of each experiment as a result of the formation of acetic acid as one of the reaction products. It may also be concluded that neither acetic acid nor acetate ion participates explicitly in the rate controlling step of the reaction.

Homogeneous Character of the Reaction

It was considered of particular importance to establish that the surface of the stainless steel autoclave was without catalytic effect on the reaction. An experiment was therefore made in which 20 gm. per liter of similar stainless steel, in the form of powder, was added to the solution. The surface area of this powder was estimated to be about 100 sq. cm. per gm. The total area of the added powder was thus at least five times as great as the surface area of

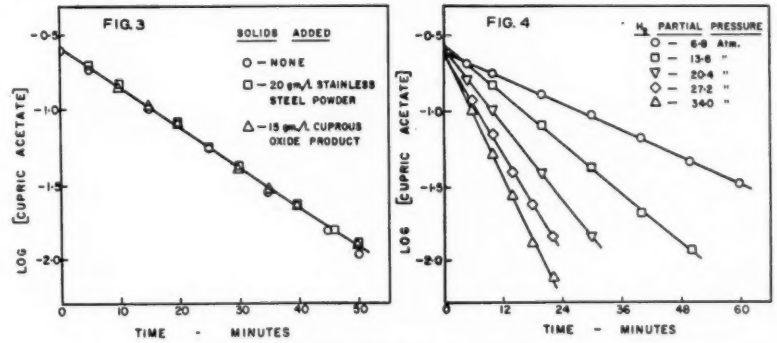


FIG. 3. Effect of surface on the rate.

FIG. 4. First order rate plots at different partial pressures of hydrogen. NaOAc, 0.25 M./liter. HOAc, 0.44 M./liter. Temperature, 130°C.

the autoclave normally in contact with the solution. Fig. 3 shows that, within experimental accuracy, the addition of this powder had no effect on the rate.

The results of a similar experiment in which 15 gm. per liter of cuprous oxide powder, the product from an earlier run, was added to the solution, are also depicted in Fig. 3. Again no effect on the rate could be detected.

These results provide direct confirmation of the homogeneous character of the reaction.

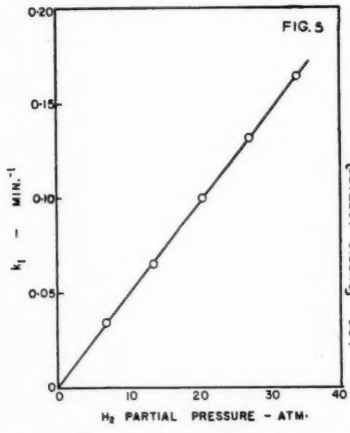
Effect of Hydrogen Partial Pressure

Fig. 4 shows the rate curves for a series of experiments in which the partial pressure of hydrogen was varied from 6.8 to 34.0 atm. The results are summarized in Fig. 5 where the rate is plotted against the hydrogen partial pressure. It is seen that the first order rate constant, k_1, is directly proportional to the partial pressure, P_{H_2}. Since the solubility of hydrogen in most aqueous solutions obeys Henry's law over this range of pressures (22), this relation also implies that k_1 is proportional to the concentration of molecular hydrogen in solution, $[H_2]$.

A new bimolecular rate constant, k_2, which is independent of the concentrations of both cupric acetate and hydrogen may thus be defined by the relation,

$$k_1 = k_2[H_2] = k_2 \alpha P_{H_2} \qquad [2]$$

where α is Henry's constant, denoting the solubility of H_2.



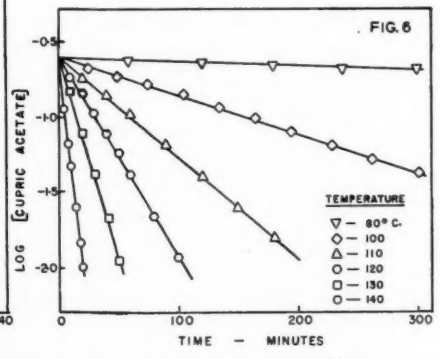


FIG. 5. Dependence of the rate on hydrogen partial pressure at 130°C.

FIG. 6. First order plots at different temperatures. NaOAc, 0.25 M./liter. HOAc, 0.44 M./liter. H_2 partial pressure, 13.6 atm.

The rate of reaction of cupric acetate can be expressed in terms of k_2 as follows:

$$-d[Cu(OAc)_2]/dt = k_2[Cu(OAc)_2][H_2]. \qquad [3]$$

Values of α have not been determined for cupric acetate solutions, but the corresponding value of α denoting the solubility of H_2 in pure water is known

to be 7.14×10^{-4} moles atm.$^{-1}$ liter^{-1} and to remain nearly constant with temperature over the range 60° to 100° C. where some of these experiments were conducted (22). Such determinations as have been made of the effect of acetic acid and various salts on the solubility of hydrogen in water (22) suggest that for solutions of the composition used in these experiments (i.e., approximately 0.5 *M* HOAc and 0.5 *M* NaOAc or NH_4OAc), α would be about 10% lower than for pure water or approximately 6.4×10^{-4} moles atm.$^{-1}$ liter^{-1}. It is believed that negligible error is introduced by assuming this value for the purpose of the present calculations.

Dependence of the Rate on Temperature

Rate curves for a series of experiments at temperatures ranging from 80° to 140° C. are given in Fig. 6. A good Arrhenius plot, shown in Fig. 7, was ob-

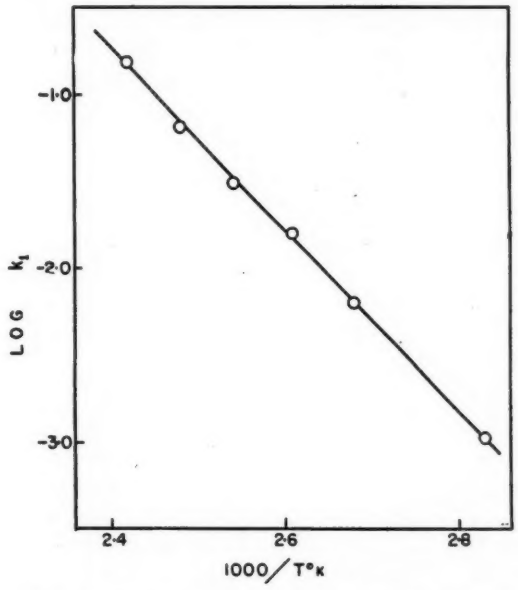


FIG. 7. Arrhenius plot for the reaction between cupric acetate and hydrogen. H_2 partial pressure, 13.6 atm.

tained when log k_1 was plotted against $1/T$. The activation energy, E, estimated from the slope of this plot using the Arrhenius relation, is 24200 ± 800 cal. per mole.

If the solubility of hydrogen is taken to be independent of temperature, this activation energy can also be associated with the bimolecular rate constant, k_2. Assuming α to have the value, 6.4×10^{-4} moles atm.$^{-1}$ liter^{-1}, k_2 is given by:

$$k_2 = 9.6 \times 10^{13} \exp\left[\frac{-24200}{RT}\right] \text{liter mole}^{-1} \text{ min.}^{-1} \qquad [4]$$

DISCUSSION

Mechanism of the Reaction

The kinetic results suggest that the rate determining step of the reaction is a bimolecular process involving one molecule of cupric acetate and one molecule of hydrogen. This step must lead to the formation of a complex in which the hydrogen has become activated so that its subsequent dissociation or reaction with another molecule of cupric acetate to give the observed reaction products is rapid. Such a sequence of steps may be represented as follows:

$$\text{1. } Cu(OAc)_2 + H_2 \xrightarrow[\text{slow}]{k} Cu(OAc)_2.H_2. \qquad [5]$$

$$\text{2. } Cu(OAc)_2.H_2 + Cu(OAc)_2 + H_2O \xrightarrow[\text{fast}]{} Cu_2O + 4\ HOAc. \qquad [6]$$

$$\text{Over-all reaction: } 2Cu(OAc)_2 + H_2 + H_2O \xrightarrow{k_2} Cu_2O + 4\ HOAc$$

The first step in this sequence is considered to be rate determining. The rate constant for this step, k, is related to that for the over-all reaction, k_2, as follows:

$$2k = k_2. \qquad [7]$$

The factor, 2, in this expression reflects the fact that only one molecule of cupric acetate is involved in the rate determining step while two molecules are involved in the equation from the over-all reaction.

Combining equations [4] and [7] gives the following expression for k:

$$k = 4.8 \times 10^{13} \exp\left[\frac{-24200}{RT}\right] \text{liter mole}^{-1} \text{ min.}^{-1} \qquad [8]$$

The value 4.8×10^{13} liter mole^{-1} min.$^{-1}$ for the Arrhenius frequency factor in this equation corresponds to an activation entropy, $\Delta S_c^{\ddagger}$, of -6.5 e.u. at 100° C. (9). These values are normal (15, 20) for a simple bimolecular reaction in solution, such as that represented by Equation [5]. This provides further support for the mechanism and rate determining steps which have been postulated above.

Nature of the Reactive Species

In the preceding discussion the reaction has been represented as involving undissociated $Cu(OAc)_2$ molecules rather than simple cupric ions or other cupric complexes. This appears to be consistent with the kinetic results taken in conjunction with independent measurements of the dissociation constants of cupric acetate (18). These measurements indicate that in solutions of the composition used in these experiments, cupric acetate is predominantly undissociated. The degree of dissociation to $CuOAc^+$ ranges from about 10% at the highest NaOAc concentration of 0.75 M./liter to about 25% at the lowest concentration of 0.25 M./liter. The dissociation to Cu^{++} is negligible. The insensitiveness of the rate to the concentration of acetate ion within this range and the magnitude of the frequency factor then provide fairly strong indication

that the observed reaction is due predominantly to the undissociated cupric acetate molecules, with other cupric species making only a minor contribution. The low concentrations of these species and the limited accuracy of the measurements make it difficult to evaluate this contribution quantitatively.

Similar considerations discourage the suggestion that cuprous acetate, which may be formed as an intermediate, has an appreciable catalytic influence on the reaction. Cuprous acetate is unstable in aqueous solution where it is hydrolyzed and precipitated quantitatively as cuprous oxide (23). This was found to be the case for the solutions used in the present study and it may be concluded that only trace concentrations of cuprous acetate were present in these solutions during reaction. Such limiting concentrations would be highly variable, and particularly sensitive to the pH and acetate ion content of the solution. Any reaction mechanism in which an important catalytic influence is attributed to cuprous acetate would thus appear to be inconsistent with the observed kinetics. This is of interest in view of earlier work which indicated that cuprous acetate activates hydrogen homogeneously in quinoline solution (4, 5, 24). The two systems appear to be unrelated.

It is of further interest that the reaction does not appear to involve a dimeric complex incorporating two copper atoms. There has previously been evidence for only two other homogeneous hydrogenation reactions, in each of which the effective catalyst was apparently a dimeric molecule containing two metal atoms, i.e., $Cu_2(OAc)_2$ and $Co_2(CO)_8$. It has been suggested that, in order to be capable of activating molecular hydrogen homogeneously, a molecule must possess such a dimeric configuration which allows the two hydrogen atoms to become simultaneously bonded to metal atoms (24). However, the results of the present study fail to support this view.

CONCLUSIONS

Cupric acetate is reduced homogeneously by hydrogen in aqueous solution. The kinetic data which were obtained in this investigation have permitted only the general features of the mechanism and the sequence of steps involved in this reaction to be deduced. The detailed configuration of the complex formed by interaction of hydrogen and cupric acetate and the nature of the forces which stabilize this complex and thus contribute to the activation of the hydrogen remain to be elucidated.

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CHLORINE ISOTOPE EFFECT IN REACTIONS OF *TERT*-BUTYL CHLORIDE[1]

By Rosalie M. Bartholomew, F. Brown, and M. Lounsbury

ABSTRACT

When *tert*-butyl chloride reacts with either alcoholic silver nitrate or aqueous alcoholic sodium hydroxide the Cl^{35} compound reacts faster than the Cl^{37} compound. The ratio of the rates of reaction is $1.008^{+0.002}_{-0.001}$.

INTRODUCTION

A previous publication (1) has summarized some experiments showing that when *tert*-butyl chloride reacts with ethyl alcoholic silver nitrate solution, the Cl^{35} compound reacts faster than the Cl^{37} compound. This paper describes these experiments in more detail, together with some further experiments in which the chloride was allowed to react with aqueous alcoholic sodium hydroxide solution.

The reaction being studied is essentially the same in both series of experiments. The rate controlling step is the reaction:

$$C_4H_9Cl \rightleftharpoons C_4H_9^+ + Cl^-.$$

In the presence of silver nitrate the back reaction is prevented because the chloride ion is removed as silver chloride; the $C_4H_9^+$ ion reacts rapidly with the solvent to produce *tert*-butyl-ethyl-ether:

$$C_4H_9^+ + C_2H_5OH \longrightarrow C_4H_9OC_2H_5 + H^+.$$

When aqueous alcoholic sodium hydroxide is the medium, the $C_4H_9^+$ ion again reacts with the solvent or with the hydroxyl or ethoxide ions so that *tert*-butyl alcohol or *tert*-butyl-ethyl-ether is produced. The back reaction is prevented by the basic nature of the solution, since neither *tert*-butyl alcohol nor *tert*-butyl-ethyl-ether react with chloride ion in the absence of acid. For a summary of the mechanism of the reactions of alkyl chlorides, see Reference 4.

In the first series of experiments (1) the *tert*-butyl chloride was allowed to react with alcoholic silver nitrate solution ($M/10$) at room temperature. By means of three separate experiments the silver chloride arising from reaction of (*a*) the *first* 35%, (*b*) the *last* 5%, and (*c*) the whole of the *tert*-butyl chloride was isolated. The isotopic composition of the chlorine in these samples was determined mass spectrometrically after conversion of the silver chloride to chlorine gas. In the second series of experiments the *tert*-butyl chloride was allowed to react with 50% aqueous alcoholic sodium hydroxide ($M/10$) at room temperature. Once again the chloride ion formed by reaction of (*a*) the *first* 10% and (*b*) the *last* 7.5% was isolated and the isotopic composition determined.

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In all cases the extent of the reaction was measured by gravimetric analysis. By comparing the Cl^{35}/Cl^{37} ratios in the various samples with that in the original *tert*-butyl chloride (obtained from the experiment in which all of the chloride was allowed to react with silver nitrate) the relative rates of reaction k^{35}/k^{37} were obtained.

EXPERIMENTAL

The *tert*-butyl chloride used was obtained from commercial stock of boiling point 49.5–50.5°C. and redistilled before use. The portion used had a boiling point which was constant within ±0.25°C. The alcoholic silver nitrate was $M/10$ in 98% ethyl alcohol. The aqueous alcoholic sodium hydroxide was $M/10$ in a mixture of equal volumes of water and 98% ethyl alcohol.

Reactions with Silver Nitrate Solution

The "35%" reaction.—*Tert*-butyl chloride (2.0 ml., 1.69 gm.) was added to alcoholic silver nitrate solution ($M/10$, 200 ml.) at room temperature (about 20°C.) and the solution shaken until the precipitated silver chloride just coagulated (about five minutes). It was then filtered as rapidly as possible through a "Buckner" funnel and the precipitate washed with alcohol. This precipitate was dissolved in strong ammonia solution and reprecipitated by adding nitric acid. The precipitate was then collected in a weighed sintered glass crucible, dried at 110°C., and weighed. It was found that 34.8% of the *tert*-butyl chloride had reacted. It would have been better to have had a much smaller percentage reaction but five minutes was the minimum time required for the precipitate to coagulate sufficiently for effective filtration.

The "last 5%" reaction.—The reaction mixture was as above; the reaction was allowed to proceed for one hour, then the precipitate was filtered off and discarded. The filtered reaction mixture was then allowed to continue reacting overnight and the silver chloride produced was isolated and weighed as before. This silver chloride corresponded to 5.2% reaction of the *tert*-butyl chloride, i.e. 94.8% had reacted when the initial precipitate was rejected.

The "100%" reaction.—The above experiments were repeated except that the mixture was allowed to react for several hours, which is sufficient to bring about complete reaction and the *whole* of the precipitate was isolated as described above.

The Reactions with Aqueous Alcoholic Sodium Hydroxide Solution

The "10%" reaction.—*Tert*-butyl chloride (2.0 ml., 1.69 gm.) was added to aqueous alcoholic sodium hydroxide ($M/10$, 200 ml.) at room temperature (about 20°C.) and the solution left for 10 min. The solution was then extracted three times with benzene, and the benzene layer was rejected (to remove unreacted *tert*-butyl chloride). The aqueous alcohol phase was diluted with an equal volume of water and extracted with benzene again (the benzene being rejected). The aqueous phase now contained the sodium chloride formed by partial reaction of the *tert*-butyl chloride. The solution was acidified with nitric acid and the chloride determined as silver chloride; 10.2% of the *tert*-butyl chloride had reacted.

The "last 7.5%" reaction.—The reactants were as above. After two and one half hours' reaction the solution was extracted twice with benzene, and the aqueous alcohol phase rejected. The benzene layer (containing the unreacted *tert*-butyl chloride) was washed quickly with ice-cold water (with rejection of the aqueous washings) and then boiled under reflux with 50 ml. of $M/10$ aqueous sodium hydroxide for several hours. The resulting mixture was then cooled and the benzene layer was rejected. The aqueous solution now contained the chloride ion (as sodium chloride) corresponding to the *tert*-butyl chloride which had been unreacted at the time of the original benzene extraction. This chloride ion was converted to silver chloride by the standard procedure of gravimetric analysis and weighed. It corresponded to 7.53% of the original *tert*-butyl chloride, i.e. 92.47% had reacted at the time of the initial benzene extraction.

Conversion of Silver Chloride to Chlorine Gas

The various samples of silver chloride obtained as above were converted to chlorine gas for mass spectrometric analysis. The silver chloride was dissolved in strong ammonia solution and the silver removed by precipitation with hydrogen sulphide. The solution was evaporated just to dryness (with the occasional addition of a few drops of ammonia solution) leaving a residue of ammonium chloride. The dried ammonium chloride was heated with concentrated sulphuric acid and, by means of a stream of nitrogen, the hydrogen chloride thus evolved was swept through a bubbler containing a little cold water. The aqueous hydrochloric acid was converted to chlorine gas by persulphate oxidation (2) in a stream of helium. The chlorine gas was frozen from the helium stream into a trap cooled in liquid nitrogen and transferred to a vacuum line where the helium was removed. The chlorine was dried over phosphorus pentoxide for 15 min. and transferred to the mass spectrometer sampling bulbs.

Mass Spectrometry

A 90°-deflection, 6-in. radius mass spectrometer (3) was used for the isotopic analysis of the chlorine gas. A silicone oil diffuson pump was used in the gas inlet system, and apiezon high vacuum grease was used for stopcocks and ground joints. The fore-leak pressure was adjusted by means of an evacuated expansion bulb. The mass spectrum was scanned magnetically and recorded with a Leeds and Northrup Speedomax Type G.

The mass spectrometer can exhibit a memory effect in the analysis of chlorine gas. However, if the samples are not widely different in their isotopic abundances, as is the case here, then the error arising from memory effect is small.

The two stable isotopes of chlorine combine to form the following molecular species:

Mass	Composition
70	$Cl^{35}Cl^{35}$
72	$Cl^{35}Cl^{37}$
74	$Cl^{37}Cl^{37}$

The isotopic abundance ratio is given by:

$$\frac{Cl^{35}}{Cl^{37}} = \frac{2(70)+(72)}{2(74)+(72)}$$

where (70) is the height of the mass 70 peak, and similarly for the others.

RESULTS

The relative rates of reaction for *tert*-butyl chloride Cl^{35} and Cl^{37} can be calculated from the results in two ways:

A. The isotopic composition of the chloride ion obtained by partial reaction of the *tert*-butyl chloride, i.e. that from the "first" portion of the reaction, can be compared with the isotopic composition of the chlorine in the original *tert*-butyl chloride.

B. Alternatively, the chlorine in the *tert*-butyl chloride which remains after partial reaction, i.e. that from the "last" portion, can be compared with the original. The isotope effect is calculated by treating the two isotopically distinguishable *tert*-butyl chlorides as two species undergoing separate first order reactions under identical reaction conditions.

The corresponding formulae are:—

$$[A] \qquad \frac{k^{35}}{k^{37}} = \frac{\ln[F_1^{35}/(F_1^{35}-pF_2^{35})]}{\ln[F_1^{37}/(F_1^{37}-pF_2^{37})]}$$

where:

k^{35}/k^{37} is the ratio of the rate constants;

F_1^{35} and F_1^{37} are the fractions of Cl^{35} and Cl^{37} in the chlorine of the original *tert*-butyl chloride—so that, if Cl^{35}/Cl^{37} is the measured ratio of isotopic abundances, then:

$$F_1^{35} = \frac{Cl^{35}/Cl^{37}}{1+Cl^{35}/Cl^{37}} \text{ and } F_1^{37} = \frac{1}{1+Cl^{35}/Cl^{37}};$$

F_2^{35} and F_2^{37} are the similar quantities for the chloride ion *produced* by partial reaction;

and p is the fraction of the *tert*-butyl chloride reacted.

$$[B] \qquad \frac{k^{35}}{k^{37}} = \frac{\ln[F_1^{35}/(1-p)F_3^{35}]}{\ln[F_1^{37}/(1-p)F_3^{37}]}$$

where:

F_3^{35} and F_3^{37} are for the chlorine in the *tert*-butyl chloride which *remains* after partial reaction;

and $(1-p)$ is the fraction remaining unreacted.

The results and calculated isotope effects are summarized in Table I.

In each case, the error shown for the isotopic abundance ratio Cl^{35}/Cl^{37} is the standard deviation of the individual spectrograms from their mean. The errors shown for the ratios of rate constants k^{35}/k^{37} are calculated on the basis of the errors in Cl^{35}/Cl^{37} ratios. Errors arising from the mass spectrometer memory effect are equivalent to a cross contamination of samples which is certainly less than 10% and is probably in the order of 2%. Any cross con-

TABLE I
SUMMARY OF RESULTS

	Cl^{35}/Cl^{37}	k^{35}/k^{37}
Reaction between C_4H_9Cl and $AgNO_3$ in alcohol		
(1) Chlorine from first 34.8% reaction	3.104±0.003	1.007±0.003
(2) Chlorine from 100% reaction	3.087±0.003	
(3) Chlorine from last 5.2% reaction	3.019±0.005	1.008±0.001
Reaction between C_4H_9Cl and NaOH in aqueous alcohol		
(4) Chlorine from first 10.2% reaction	3.113±0.003	1.009±0.002
(5) Chlorine from 100% reaction (taken to be same as (2) above)	3.087±0.003	
(6) Chlorine from last 7.53% reaction	3.035±0.004	1.007±0.001

tamination of sample tends to lessen the measured isotope effect because it makes the isotopic compositions of the various samples appear to be more nearly identical than they in fact are. A cross contamination of 10% would cause the observed k^{35}/k^{37} ratio be to be about 0.001 low. Allowing for this possibility the isotope effect may therefore be taken as $k^{35}/k^{37} = 1.008^{+0.002}_{-0.001}$.

CONCLUSION

The isotope effect is small but significant and is in the expected direction i.e., the heavier isotope of chlorine is bound more firmly to the carbon atom than is the lighter isotope and consequently undergoes bond breaking reactions less rapidly. There is no measurable difference in the effect for the two sets of reaction conditions.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
I. CODEINE MONOHYDRATE, CODEINE (ANHYDROUS), DIHYDROCODEINONE[1]

By W. H. Barnes and W. J. Forsyth*

This is the first of a series of short notes on the unit cell constants, space groups, and indexed X-ray diffraction powder data for a number of narcotics (largely opium alkaloids and some of their salts). The determinations were made to authenticate a few of the powder patterns obtained in a recent survey of 83 narcotics (3) and as a preliminary step in the choice of suitable compounds for detailed structure investigation.

The unit cell and space group data were collected by the Buerger precession method (4), films were measured with the standard measuring device (5), and corrections for film shrinkage (2) were applied. Unless specifically stated otherwise, all precession photographs were taken with either Cu K_α radiation ($\lambda = 1.5418$ Å) or Co K_α radiation ($\lambda = 1.7902$ Å). Densities were determined by flotation of clear crystals in binary solutions of carbon tetrachloride or methylene iodide with acetone or benzene, as dictated by the particular compound involved, and all measurements were made at a temperature of 21–23° C.

The techniques employed for the powder photographs have been described in detail elsewhere (1, 3) where the complete powder data will be found. In the present notes, only those values of the observed spacings (generally for $d > 3$ Å) are repeated for which it seems useful to record the indices of the corresponding planes. Although indexing was continued to lower values of d than the smallest appearing in the present Tables of powder data, coincidence of reflections becomes too numerous at the higher 2θ angles to make the inclusion of the indices of any value. In all cases, Co K_α radiation ($\lambda = 1.790$ Å) was employed for the powder photographs and the apparatus "cut-off" was 20 Å; film shrinkage corrections were not significant, and, therefore, were not applied. After indexing, the powder films were re-examined on the powder-film measuring device and an estimate was made of the reflections that might reasonably be expected to have contributed to a given line on the photograph; such reflections are bracketed in the columns of d(Calc.) in the tables of powder data. Reflections probably present, but with $I/I_1 < 1$, are indicated by an asterisk in the columns of d(Obs.). Lines which appeared to be broader than the general average for a given pattern are designated B (broad) and BB (very broad) in the columns of I/I_1.

Unless otherwise acknowledged, all substances (some of commercial and some of laboratory origin) which are the subject of the present series of notes

[1]*Issued as N.R.C. No. 3358.*
**Now with the Aluminum Company of Canada, Arvida, Que.*

TABLE I

SINGLE CRYSTAL DATA FOR CODEINE MONOHYDRATE, CODEINE (ANHYDROUS), AND DIHYDROCODEINONE

	Codeine monohydrate	Codeine (anhydrous)	Dihydrocodeinone
a	12.15 Å	13.68 Å	14.02 Å
b	12.63 Å	14.72 Å	14.64 Å
c	10.51 Å	7.48_7 Å	7.23_5 Å
S.G.	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Z	4 molecules/cell	4 molecules/cell	4 molecules/cell
ρ (calc.)	1.307 gm./ml.	1.318 gm./ml.	1.338 gm./ml.
ρ (obs.)	1.295 gm./ml.	1.310 gm./ml.	1.342 gm./ml.

TABLE II

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.00$ Å) FOR CODEINE MONOHYDRATE

I/I_1	d(Å) Obs.	d(Å) Calc.	hkl	I/I_1	d(Å) Obs.	d(Å) Calc.	hkl
90	8.76	8.75	110	—	—	3.79	212
20	8.11	8.08	011			3.78	301
	*	7.95	101	30	3.72	3.72	131
50	6.73	6.73	111		*	3.62	311
20	6.32	6.31	020	1	3.44	3.46	230
—	—	6.07	200			3.41	320
25	5.59	5.60	120	30	3.36	3.38	013
	*	5.47	210			3.37	103
		5.41	021			3.36	222
40	5.25	5.26	002, 201	15	3.30	3.29	032, 231
		4.94	121		*	3.25	113
100	4.85	4.85	012, 211			3.24	321
		4.82	102			3.21	302
1	4.52	4.51	112		*	3.17	132
8	4.37	4.38	220			3.16	040
20	4.05	4.04	022, 221			3.11	312
10	3.96	3.98	130			3.06	023
		3.97	202	2B	3.05	3.05	140
	*	3.91	031			3.04	400, 203
15	3.85	3.86	310			3.02	041
		3.83	122				

TABLE III

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.00$ Å) FOR CODEINE (ANHYDROUS) AND DIHYDROCODEINONE

Codeine (anhydrous)				Dihydrocodeinone			
I/I_1	d(Å)		*hkl*	I/I_1	d(Å)		*hkl*
	Obs.	Calc.			Obs.	Calc.	
15	10.1	10.0	110	15	10.1	10.1	110
3	7.34	7.36	020	3	7.33	7.32	020
30	6.85	6.84	200	25	7.02	7.01	200
10B	6.63	6.67	011	100	6.49	6.49	011, 120
		6.57	101	3	6.38	6.43	101
100	6.47	6.48	120			6.32	210
20	6.20	6.20	210	10	5.87	5.89	111
15	6.00	6.00	111	25	5.14	5.15	021
40	5.23	5.25	021	25	5.02	5.06	220
40	5.04	5.05	201			5.03	201
		5.01	220	40	4.83	4.83	121
60	4.89	4.90	121	3	4.76	4.76	211
30	4.77	4.78	211	—	—	4.61	130
	*	4.62	130		*	4.45	310
	*	4.36	310	3	4.15	4.15	221
5B	4.12	4.16	221	5	4.04	4.05	031
		4.10	031	—	—	4.01	230
—	—	3.99	230			3.94	320
		3.93	131	15	3.90	3.93	301
45	3.88	3.89	301			3.89	131
		3.88	320	75	3.78	3.79	311
75	3.77	3.76	311	5B	3.64	3.66	040
		3.74	002			3.62	002
10	3.67	3.68	040			3.54	140
		3.63	012	10	3.53	3.51	012, 400
—	—	3.61	102			3.50	102, 231
		3.55	140	—	—	3.46	321
15B	3.52	3.52	231	20	3.40	3.41	112, 410
		3.51	112			3.38	330
15	3.44	3.44	321			3.27	041
		3.42	400	1	3.25	3.25	240
5	3.34	3.34	022, 330			3.24	022
		3.33	410		*	3.22	202
—	—	3.30	041			3.18	141
		3.28	202	18	3.16	3.16	122, 420
25B	3.23	3.24	122, 240			3.15	401
		3.21	141, 212			3.14	212
1	3.10	3.11	401	10	3.07	3.08	411
		3.10	420			3.06	331
20	3.05	3.05	331				
		3.04	411				

were kindly supplied by Dr. C. G. Farmilo. Their authentication has been discussed elsewhere (8).

Data for codeine monohydrate, $C_{18}H_{21}O_3N \cdot H_2O$, codeine (anhydrous free base), $C_{18}H_{21}O_3N$, and dihydrocodeinone (dicodide), $C_{18}H_{21}O_3N$, are presented in Tables I, II, and III. Codeine was crystallized from water as the monohydrate, and from absolute ethanol as the anhydrous base. Crystals of the hydrate gave a positive piezoelectric test. They are efflorescent and gradually become opaque, even in a closed vial, without losing their external form; such

individual pseudomorphs give excellent powder patterns of anhydrous codeine without crushing. Specimens of codeine, therefore, sometimes represent mixtures of the hydrated and the anhydrous forms and this fact should be borne in mind when X-ray diffraction powder patterns are employed for the identification of codeine base. In the present investigation the monohydrate and the anhydrous phase were differentiated initially on the basis of the axial ratios deduced from the single-crystal data (Table I), thus, $a:b:c = 0.9621:1:0.8326$ (compare, 0.9595: 1: 0.8346) (9, No. 2060) for codeine monohydrate, and $a:b:c = 0.9291:1:0.5085$ (compare, 0.9298: 1: 0.5087) (9, No. 2059) for anhydrous codeine.

The ring to which the alcoholic OH is attached in codeine (morphine methyl ether), $CH_3O \cdot C_{17}H_{17}ON \cdot OH$, contains one double bond; in dihydrocodeinone, $CH_3O \cdot C_{17}H_{18}ON \cdot O$, this ring is fully saturated and a keto-oxygen replaces the OH; otherwise the structural formulae of the two compounds are identical. The crystal structures of both, therefore, may be expected to be very similar and this is supported by the single-crystal data of Table I and the powder data of Table II.

Castelliz and Halla (6) have reported the space group of codeine and of "β-methyl-morphimetin" (β-methylmorphimethine (10)) as $P2_12_12$. For codeine they found $a = 27.70$, $b = 29.80$, $c = 7.59$ Å (probably kX units). That the material they examined really was codeine (anhydrous free base), and that their unit cell orientation is the same as that on which the present data are based, is indicated (1) by the axial ratio calculated from their cell dimensions, thus, $a:b:c = 0.9295:1:0.2547$ (i.e., 0.5094/2), (2) by the fact that if their values for a and b are each divided by 2, the three axial lengths are similar (actually 1% higher in each case) to the corresponding ones obtained in the present study (see Table I), and (3) their observed density is 1.3068 compared with the present value (observed) of 1.310. Why they should have doubled the lengths of both a and b and missed the screw-axis along c is not clear. The fact that they found 16 molecules per cell, thus requiring (as they realized) four sets of general fourfold positions, should have suggested that the cell as measured probably was too large to be the true one. It is unfortunate that some of these data for codeine and for β-methylmorphimethine should have found their way into *Crystal Data* (7), particularly since there has been some confusion in the listings. Thus the prefix "beta-" has somehow become attached to "Codeine" in the Name Index (7, p. 677) and (under space group D_2^3—$P2_12_12$) in the Main Table (7, p. 27); this is particularly misleading because "β-codeine" is an alternative name for an isomer of codeine, namely, neopine. Apart from this, the numerical data of Castelliz and Halla (6) for codeine are not included in the Determinative Tables. On the other hand, β-methylmorphimethine appears as "beta-Methyl-moryhimetin" [*sic*] not only in the Name Index (7, p. 697) but also, with the complete data of Castelliz and Halla (6), in the Determinative Tables (7, p. 287). These data probably are no more reliable than are those for codeine; in fact, the number of molecules per cell is given in the original note (6) as "16 ($\sim$ 17)". Finally, β-methylmorphimethine does not appear with codeine in the Main Table (7, p. 27).

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
II. *dl*-METHADONE HYDROCHLORIDE, *dl*-METHADONE HYDROBROMIDE[1]

BY W. H. BARNES AND W. J. FORSYTH*

The unit cell constants, space group, and X-ray diffraction powder data for *dl*-methadone (amidone: 6-dimethyl-4,4-diphenyl-3-heptanone) hydrochloride and for *dl*-methadone hydrobromide were determined by the methods outlined in Part I of this series of notes (1); the results are shown in Tables I and II.

Both salts were recrystallized from distilled water. Some difficulty was experienced with one laboratory preparation of the hydrobromide (2) apparently because of mixed crystal formation with a significant proportion of the hydrochloride as contaminant. The purity of the crystals used for the X-ray diffraction data reported, however, was established by converting the salt to the free base with concentrated ammonia solution and obtaining the powder

TABLE I

SINGLE CRYSTAL DATA FOR *dl*-METHADONE HYDROCHLORIDE AND FOR *dl*-METHADONE HYDROBROMIDE

	dl-Methadone hydrochloride	*dl* Methadone hydrobromide
a	16.26 Å	16.44 Å
b	9.76 Å	9.81 Å
c	25.74 Å	26.29 Å
β	106°05′	106°52′
S.G.	Cc or $C2/c$	Cc or $C2/c$
Z	8 molecules/cell	8 molecules/cell
ρ (calc.)	1.171 gm./ml.	1.278 gm./ml.
ρ (obs.)	1.178 gm./ml.	1.287 gm./ml.

[1]*Issued as N.R.C. No. 3359.*
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TABLE II

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.60$ Å) FOR *dl*-METHADONE HYDROCHLORIDE AND *dl*-METHADONE HYDROBROMIDE

dl-Methadone hydrochloride				*dl*-Methadone hydrobromide			
I/I_1	d(Å) Obs.	d(Å) Calc.	*hkl*	I/I_1	d(Å) Obs.	d(Å) Calc.	*hkl*
25	12.4	12.4	002	30	12.6	12.6	002
10	8.25	8.28	110	25	8.27	8.33	110
		8.22	$11\bar{1}$			8.29	$11\bar{1}$
5	7.87	7.81	200		*	7.87	200
		7.63	$20\bar{2}$	2	7.75	7.76	$20\bar{2}$
90	7.50	7.52	111	90	7.53	7.56	111
		7.40	$11\bar{2}$			7.49	$11\bar{2}$
70	6.48	6.46	112	80	6.48	6.50	112
	*	6.32	$11\bar{3}$			6.42	$11\bar{3}$
1	6.20	6.18	004	1	6.25	6.29	004
20	5.92	5.91	202	10	5.90	5.94	202
5	5.70	5.67	$20\bar{4}$	20	5.80	5.81	$20\bar{4}$
	*	5.46	$11\bar{3}$	20	5.47	5.50	$11\bar{3}$
—	—	5.34	$11\bar{4}$			5.44	$11\bar{4}$
	*	4.88	020	—	—	4.91	020
		4.79	$02\bar{1}$	—	—	4.81	$02\bar{1}$
30	4.72	4.73	$31\bar{1}$	50	4.76	4.77	$31\bar{1}$
		4.70	$31\bar{2}$			4.75	$31\bar{2}$
—	—	4.64	$11\bar{4}$	—	—	4.68	$11\bar{4}$
		4.60	310			4.63	$310, 11\bar{5}$
100	4.57	4.55	$11\bar{5}$	100	4.60	4.58	$31\bar{3}$
		4.54	022			4.57	022
		4.51	$31\bar{3}$	45	4.34	4.36	311
40	4.34	4.33	311			4.34	$20\bar{4}$
		4.30	204		*	4.29	$31\bar{4}$
		4.21	$31\bar{4}$		*	4.25	$20\bar{6}$
3	4.20	4.20	$02\bar{3}$			4.23	$02\bar{3}$
		4.18	$22\bar{1}$			4.21	$22\bar{1}$
		4.15	$20\bar{6}$	20	4.17	4.19	006
20	4.14	4.14	220			4.16	220
		4.12	006			4.15	$22\bar{2}$
		4.11	$22\bar{2}$		*	4.11	$40\bar{2}$
		4.06	$40\bar{2}$			4.04	115
20	4.00	4.00	115, 312			4.02	312
		3.99	221			4.01	221
	*	3.94	$22\bar{3}$	40B	3.98	4.00	$11\bar{6}$
		3.93	$11\bar{6}$			3.98	$22\bar{3}$
		3.91	400			3.95	$31\bar{5}$
20	3.87	3.87	$31\bar{5}$			3.93	400
		3.83	024			3.88	$40\bar{4}$
		3.81	$40\bar{4}$	—	—	3.87	024
		3.76	$22\bar{2}$			3.78	$22\bar{2}$
5BB	3.71	3.70	$22\bar{4}$	5	3.77	3.75	$22\bar{4}$
		3.65	313	5	3.67	3.67	313

pattern of the liberated ammonium salt. The latter showed excellent agreement with precision data (4) for NH_4Br. The density calculated on the basis of the single-crystal data (assuming pure methadone hydrochloride) also was in satisfactory agreement with that measured experimentally for these crystals.

A curious anomaly was encountered in the case of the hydrochloride. Independent determinations of the unit cell constants on separate crystals were in agreement to better than 0.2%, and the calculated density (assuming pure methadone hydrochloride) was 1.171 gm./ml. Three independent measure-

ments by different individuals on separate groups of crystals from the same preparation, however, while in satisfactory mutual agreement, gave an average density of 1.207 gm./ml. The difference could be explained by replacement of approximately one third of the Cl atoms with Br atoms, or by the presence of $\frac{1}{2}$ mole H_2O per mole anhydrous salt. The first possibility is most unlikely because the powder pattern of the ammonium salt obtained by the action of ammonia (2) was in excellent agreement with precision data (4) for NH_4Cl. The second possibility is eliminated by a water-determination carried out by Mrs. P. M. Oestreicher (3). Finally, a density of 1.178 gm./ml. (mean of eight measurements) was observed for crystals from a different preparation, while the powder data from both specimens were the same within the limits of experimental error. It seems probable, therefore, that the higher density found for the first lot of crystals is real, but may be due simply to surface contamination. On the other hand, further study of the density of *dl*-methadone hydrochloride crystals from different preparations might be of interest.

Hubach and Jones (5) obtained some Weissenberg photographs of *dl*-methadone hydrochloride but do not report any values for the axial lengths of the unit cell. The monoclinic angle was measured with the rotating stage of the microscope as 74° (i.e., $\beta = 106°$). They found those space group extinctions which are consistent with either Cc or $C2/c$ but ruled out the twofold axis on the basis of the morphology of the crystals, thus concluding that the space group is uniquely established as Cc. On the other hand, the presence of eight molecules per cell (Table I) favors $C2/c$ unless, of course, the structural unit comprises two molecules.

The powder data of Hubach and Jones (5) (obtained with Cu K_α radiation) for *dl*-methadone hydrochloride are in very good agreement with those of Table II with the exception of a line of $d = 5.04$ Å (very weak) which cannot be a K_α line because it does not index on the basis of the single-crystal data of Table I; it agrees, however, with a K_β reflection corresponding to their strongest line of $d = 4.55$ Å. With the exception of a line of $d = 5.65$ Å (medium weak), their pattern does not contain those lines for which $I/I_1 \leqq 5$ in the present photographs, although their line of $d = 5.38$ Å (very weak), which could be indexed as $11\bar{4}$ (d(Calc.) = 5.34 Å), does not appear on the present films.

Finally, in connection with the data of Table II, it may be mentioned that the very broad line of $d = 3.71$ Å is resolved on some films into two lines of $d = 3.76$ Å and $d = 3.68$ Å, respectively.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION DATA FOR CERTAIN NARCOTICS
III. *dl*-ALPHAPRODINE HYDROCHLORIDE, *dl*-BETAPRODINE HYDROCHLORIDE[1]

By W. H. Barnes and W. J. Forsyth*

The unit cell constants, space group, and X-ray diffraction powder data for *dl*-alphaprodine (nisentil[R]; α-1,3-dimethyl-4-phenyl-4-propionoxypiperidine) hydrochloride, $C_{16}H_{23}NO_2 \cdot HCl$, and for *dl*-betaprodine hydrochloride were determined by methods previously outlined (1); the results are shown in Tables I and II.

No difficulty was experienced with the specimen of the alpha-form but that of betaprodine hydrochloride was found to consist of crystal fragments of two different types. The larger crystals were slightly elongated along *b* and were tabular on {100}. The best-developed forms were the three pinacoids so that, with β differing from 90° by 17° only, the crystals had the superficial appearance of rectangular plates under low magnification. This constituent was identified as the α-form by direct comparison of its powder pattern with that of the specimen of *dl*-alphaprodine hydrochloride. The smaller crystals also were monoclinic but were tabular on {001} with other forms so developed as to give a somewhat elongated, pseudohexagonal outline under low magnification. They were present in larger proportion in the mixture and were accepted as representing the β-form. It was not difficult, therefore, to select reasonably good individual crystals of both the α- and β-forms from the partially or wholly anhedral fragments comprising the bulk of the specimen of *dl*-betaprodine hydrochloride.

According to the method of Ziering and Lee (2), *dl*-alphaprodine hydrochloride and *dl*-betaprodine hydrochloride are separated by first crystallizing out the α-form from a solution of the two in about 600 cc. of acetone containing a little methanol. Concentrating the filtrate to 250 cc. and allowing it to stand in the ice-box overnight then gives a second crop of crystals (supposedly the

TABLE I

Single crystal data for *dl*-alphaprodine hydrochloride and for *dl*-betaprodine hydrochloride

	dl-Alphaprodine hydrochloride	*dl*-Betaprodine hydrochloride
a	15.77 Å	12.09 Å
b	8.15 Å	11.84 Å
c	13.95 Å	12.31 Å
β	107°00′	112°35′
S.G.	$P2_1/c$	$P2_1/c$
Z	4 molecules/cell	4 molecules/cell
ρ (calc.)	1.154 gm./ml.	1.216 gm./ml.
ρ (obs.)	1.167 gm./ml.	1.214 gm./ml.

[1]*Issued as N.R.C. No. 3362.*

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TABLE II

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.50$ Å) FOR *dl*-ALPHAPRODINE HYDROCHLORIDE AND *dl*-BETAPRODINE HYDROCHLORIDE

dl-Alphaprodine hydrochloride				*dl*-Betaprodine hydrochloride			
I/I_1	d(Å)		hkl	I/I_1	d(Å)		hkl
	Obs.	Calc.			Obs.	Calc.	
50	15.1	15.1	100	20	11.2	11.2	100
5	7.50	7.54	200	100	8.13	8.20	011
100	7.14	7.17	110			8.12	110
—	—	6.96	011		*	7.70	11$\bar{1}$
1	6.87	6.89	10$\bar{2}$	25	6.08	6.10	10$\bar{2}$
70	6.69	6.72	11$\bar{1}$	70	5.87	5.92	020
		6.67	002			5.88	111
80	5.96	5.98	111		*	5.68	002
		5.93	20$\bar{2}$		*	5.58	200
		5.55	21$\bar{1}$	20	5.39	5.42	11$\bar{2}$
10	5.52	5.54	210			5.36	21$\bar{1}$
		5.53	102	15	5.24	5.25	021
—	—	5.26	11$\bar{2}$			5.23	120
60	5.16	5.16	012	70	5.10	5.12	012
10	5.01	5.03	300			5.11	12$\bar{1}$
		4.79	21$\bar{2}$	—	—	5.07	20$\bar{2}$
30	4.74	4.76	211			5.05	210
		4.73	30$\bar{2}$	5	4.63	4.66	21$\bar{2}$
30	4.56	4.58	112	15	4.41	4.46	121
5	4.39	4.40	202, 31$\bar{1}$			4.42	102
25	4.27	4.28	310	40	4.23	4.25	12$\bar{2}$
		4.09	31$\bar{2}$			4.22	22$\bar{1}$
20	4.06	4.08	020			4.14	112
		4.04	11$\bar{3}$	40	4.08	4.11	211
		3.94	120			4.10	022
		3.90	013, 021			4.06	220
20	3.88		21$\bar{3}$			3.87	11$\bar{3}$, 30$\bar{2}$
		3.87	212	40B	3.82	3.85	22$\bar{2}$
		3.86	12$\bar{1}$			3.81	31$\bar{1}$
		3.81	311			3.73	031
30	3.78	3.79	40$\bar{2}$	40B	3.69	3.72	130, 300
		3.77	400			3.71	21$\bar{3}$
—	—	3.70	121			3.68	13$\bar{1}$, 31$\bar{2}$
		3.59	220, 22$\bar{1}$		*	3.61	013
60	3.58	3.56	113, 31$\bar{3}$			3.55	310
		3.55	302, 41$\bar{1}$	25	3.52	3.54	122
—	—	3.51	12$\bar{2}$			3.52	221

β-form) which is finally recrystallized three times from acetone. If the two specimens of prodine hydrochloride available for the present investigation were separated in this way, it is perhaps not surprising that the one labelled β-prodine hydrochloride should contain some of the α-isomer; this possibility should be considered in problems of identification involving prodine hydrochloride.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
IV. PROTOPINE[1]

By W. H. Barnes and W. J. Forsyth*

The unit cell constants, space group, and X-ray diffraction powder data for protopine, $C_{20}H_{19}O_5N$, were determined by methods outlined previously (1).

Three samples were examined. The first (A), from a commercial supplier, was found (2) to be a mixture of two substances of which the coarser-grained proved to be protopine. The second constituent, however, was not identified but presumably it represents another alkaloid that was not separated from the protopine during the course of the procedure employed to isolate the latter; it is not cryptopine, nor any of the other narcotics for which powder data were readily available (2) for comparison.

The other two samples (B, C) were kindly provided by Dr. L. Marion. One of these (B), in the form of a relatively fine-grained powder, had come from the same commercial source as A. The second (C), comprising good single crystals and crystal aggregates, had been extracted from *Adlumia fungosa* and authenticated as protopine by Dr. Marion.

Powder patterns from B and from crushed fragments of C were identical with each other and with the coarser-grained material of A which was responsible for the appearance of markedly spotty lines on some of the powder photographs of the mixture. Confirmation was obtained from photographs of a few of the larger fragments from mixture A which were selected and

TABLE I
Indexed X-ray diffraction powder data ($d > 4.00$ Å) for protopine

I/I_1	d(Å) Obs.	d(Å) Calc.	hkl	I/I_1	d(Å) Obs.	d(Å) Calc.	hkl
20	10.7	10.7	011	35	4.97	4.98	$11\bar{3}$
35	8.74	8.72	020			4.93	120
—	—	7.33	021	100	4.47	4.49	$13\bar{1}$
25	6.77	6.76	002			4.47	111
5	6.57	6.58	$10\bar{2}$			4.46	$12\bar{3}$
		6.54	$11\bar{1}$	—	—	4.41	032
30	6.31	6.30	012	80	4.36	4.36	013, 040
—	—	6.16	$11\bar{2}$				$13\bar{2}$
90	5.96	5.98	100	25	4.16	4.17	130
—	—	5.66	110			4.15	041
5	5.51	5.49	$12\bar{1}$	—	—	4.08	121
30B	5.30	5.34	022, 031	80	4.01	4.02	$10\bar{4}$
		5.25	$12\bar{2}$			4.00	023

[1]*Issued as N.R.C. No. 3363.*
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removed under the stereoscopic microscope and then reduced to a powder.

Precession photographs also were taken of a single clear fragment from A and of a small crystal from C. This completely established the identity of the larger particles of A as protopine and furnished data for the determination of the unit cell constants and space group.

The space group of protopine is $P\,2_1/c$; $a = 7.10_9$ Å, $b = 17.44$ Å, $c = 16.08$ Å (c chosen $> a$ to give protopine the standard (3) orientation for C_{2h}^5, unique axis b), $\beta = 122°45'$; the number of molecules per cell (Z) = 4; $\rho_{calc.} = 1.399$ gm./ml., $\rho_{obs.} = 1.393$ gm./ml.

On the basis of a morphological study by Schwantke of protopine crystals from *Chelidonium majus*, Schmidt (4) gives the axial ratio $a:b:c = 0.8992:1:?$ and $\beta = 57°19'$ (i.e., $122°41'$), the latter in excellent agreement with the present value. If the a and c of Schwantke be interchanged, his axial ratio may be compared directly with the present $a:b:c = 0.4076:1:0.9219$.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
V. PAPAVERINE, PAPAVERINE HYDROCHLORIDE[1]

By W. H. Barnes

During the compilation of X-ray diffraction powder data for the identification of a number of narcotics (3), no difficulties were encountered in obtaining reproducible photographs from papaverine (6:7-dimethoxy-1-[3′:4′-dimethoxy-benzyl] isoquinoline), $C_{20}H_{21}O_4N$, or from papaverine hydrochloride. In fact the base was selected for a demonstration of the effect of radiation wave-length on the appearance of powder photographs (1). At the time of the narcotics survey, therefore, it was not deemed essential to authenticate the powder data for either the free base or the hydrochloride from single-crystal data. During the preparation of the present series of notes (2), however, unit cell and space group data have become available (4) for both papaverine and papaverine hydrochloride and thus it now becomes of interest to index the powder patterns. The results are shown in Table I.

Van Hulle, Amelinckx, and Dekeyser (4) give the space group of papaverine as $P2_12_12_1$ with $a = 9.50$ Å, $b = 29.22$ Å, $c = 6.35$ Å, and that of papaverine hydrochloride as $P2_1/c$ with $a = 13.10$ Å, $b = 15.80$ Å, $c = 9.22$ Å, $\beta = 92°36'$. The cell dimensions were obtained from rotation and Weissenberg photographs and β (for the hydrochloride) from goniometric measurements and b-axis

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zero-level Weissenberg films. The radiation employed was Cu K_α. The values for d(Calc.) in Table I are derived from these constants.

TABLE I

INDEXED X-RAY DIFFRACTION POWDER DATA FOR PAPAVERINE ($d > 3.25$Å) AND PAPAVERINE HYDROCHLORIDE ($d > 3.65$Å)

Papaverine				Papaverine hydrochloride			
I/I_1	d(Å) Obs.	d(Å) Calc.	hkl	I/I_1	d(Å) Obs.	d(Å) Calc.	hkl
10	14.8	14.6	020		*	13.1	100
12	8.90	9.03	110	20	10.1	10.1	110
3	7.89	7.96	120	20	7.87	7.96	011
—	—	7.31	040			7.90	020
—	—	6.80	130	40	6.85	6.92	11$\bar{1}$
	*	6.21	011			6.76	120
100	5.79	5.82	021	5	6.59	6.68	111
		5.79	140			6.54	200
	*	5.32	031	15	5.93	6.05	210
		5.28	101			6.00	021
25	5.21	5.20	111	—	—	5.51	12$\bar{1}$
		4.98	150	40	5.35	5.39	121
30	4.93	4.96	121	75	5.12	5.15	21$\bar{1}$
		4.87	060			5.04	220
		4.79	041		*	4.96	211
30	4.77	4.75	200			4.89	130
—	—	4.69	210	100	4.56	4.61	002
40	4.61	4.64	131			4.57	031
20	4.48	4.52	220			4.49	22$\bar{1}$
2	4.38	4.33	160	70	4.44	4.42	012
	*	4.30	051			4.41	10$\bar{2}$
25	4.26	4.28	141			4.36	221, 300
		4.27	230	3	4.32	4.35	13$\bar{1}$
—	—	3.98	240			4.29	131
—	—	3.92	151			4.28	102
		3.86	061		*	4.24	11$\bar{2}$
85	3.87	3.82	170	3	4.20	4.20	310
—	—	3.80	201		*	4.13	112
		3.77	211	25	4.08	4.10	230
90	3.73	3.69	250	—	—	3.98	022
		3.68	221			3.95	040
5	3.65	3.65	080	—	—	3.89	31$\bar{1}$
		3.58	161			3.85	20$\bar{2}$, 12$\bar{2}$
5	3.57	3.54	231			3.82	320
15	3.51	3.49	071			3.79	23$\bar{1}$
		3.41	180	20	3.79	3.78	140
—	—	3.40	260			3.77	122
2	3.35	3.37	241			3.76	311
40	3.28	3.27	171			3.74	21$\bar{2}$
				60	3.68	3.71	231
						3.69	202

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THE EFFECT OF MEMBRANE THICKNESS IN DIALYSIS

By J. H. E. Herbst

In another investigation it was suspected that under certain conditions the thickness of the membranes in the Webcell Continuous Dialyzer, Laboratory Model (Brosites Machine Company, New York) was not a rate-controlling factor. No information on the effect of membrane thickness in continuous dialysis was found in the literature. To investigate this phenomenon further, aqueous sodium chloride and sucrose solutions (100 gm./liter) were dialyzed at various feed rates with No. 300 and No. 450 P.T. cellophane membranes. The thickness of the dry membranes was 0.00088 in. and 0.0012 in., respectively. The water feed rate was 200 ml./min. In addition, batch dialyses were carried out with the same solutions and membranes. The solutions were stirred vigorously, and the water feed rates were sufficient to render the concentration of solute in the effluent diffusate negligible. The temperature was 10–15° in all experiments. Pertinent information is given in Table I.

TABLE I
RESULTS OF DIALYSES

Type of dialysis	Solute	Membrane	Solution feed rate, ml./min.	Dialysis rate coefficient*
Continuous	Sodium chloride	300	12	4.3
			28	4.2
			40	4.6
		450	4	3.6
			12	4.8
			15	4.2
			41	3.9
	Sucrose	300	3	0.96
			4	0.82
			6	0.92
		450	4	0.59
			5	0.73
Batch	Sodium chloride	300		4.9
				4.9
		450		3.9
				3.9
	Sucrose	300		0.78
				0.91
		450		0.69
				0.71

**Grams of solute transferred per square meter of membrane per hour per gram per liter concentration difference (geometric mean).*

The usual statistical tests† indicated that there was no correlation between the solution feed rate and the dialysis rate coefficient; that, for the continuous

†*Kindly applied by Dr. D. B. DeLury.*

dialysis of sodium chloride, there was no significant difference between the dialysis rate coefficients for the two membranes; and that, for the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose, there was a significant difference between the dialysis rate coefficients for the two membranes.

Fick's law is obeyed fairly well in the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose (the ratio of the thicknesses of the dry membranes is 1.4, while the ratio of the dialysis rate coefficients is 1.4 for the continuous dialysis of sucrose, 1.3 for the batch dialysis of sodium chloride, and 1.2 for the batch dialysis of sucrose). Thus, the results indicate that in the continuous dialysis of sodium chloride, transfer to the membrane was a rate-controlling process, while, in the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose, transfer through the membrane was a rate-controlling process.

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Notes to Contributors

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(i) ***General.*** Manuscripts should be typewritten, double spaced, on paper 8½×11 in. **The original and one copy are to be submitted.** Tables (each typed on a separate sheet) and captions for the figures should be placed at the end of the manuscript. Every sheet of the manuscript should be numbered.

Style, arrangement, spelling, and abbreviations should conform to the usage of this journal. Names of all simple compounds, rather than their formulas, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed.

Manuscripts should be carefully checked before they are submitted; authors will be charged for changes made in the proof that are considered excessive.

(ii) ***Abstract.*** An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required, except in Notes.

(iii) ***References.*** References should be listed **alphabetically by authors' names,** numbered, and typed after the text. The form of the citations should be that used in this journal; in references to papers in periodicals, titles should not be given and only initial page numbers are required. All citations should be checked with the original articles and each one referred to in the text by the key number.

(iv) ***Tables.*** Tables should be numbered in roman numerals and each table referred to in the text. Titles should always be given but should be brief; column headings should be brief and descriptive matter in the tables confined to a minimum. Numerous small tables should be avoided.

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